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Note on Large Cosmic-Ray Bursts in an Unshielded Ionization Chamber

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Large cosmic-ray bursts as recorded with an unshielded ionization chamber have been found to be coincident with extensive atmospheric (Auger) showers as detected with Geiger-Müller counters. The experiments show that the bursts observed in the ionization chamber represent regions of very high particle density in an Auger shower. The integral size-frequency distribution curve of these bursts is approximated by an inverse power law with an exponent 2.15 ± 0.35.

A CARNEGIE model *C* ionization chamber[1] was used to detect cosmic-ray bursts of more than 100 particles. The chamber was completely unshielded, and it was located in the greenhouse of the Botany building on the campus so that there was little shower-producing material above or to the side of the chamber. In order to detect extensive showers, five coincidence units were used, and the G-M counters for these were arranged on light wooden racks suspended over the chamber. The units, *AA* and *BB* were high resolving power 2-fold coincident circuits (1.2 and 2.0 microseconds resolving time, respectively); *CCCC* and *DDDD* were 4-fold circuits, and *E* was a 5-fold circuit. A typical arrangement of the counters is shown in Fig. 1. Coincidences of the circuits were recorded by means of small lamps on the same photographic film as that on which the bursts were recorded. Thus a continuous photographic registration was obtained both for the bursts and for each coincidence circuit. Special care was taken to be certain that each circuit operated independently of all others, and the examination of the photographic record allowed an excellent check on the performance of the circuits.

A total of 107 bursts were observed while the counters were in operation; the number of particles in these bursts ranged up to 3000. Of the 107 bursts, at least 94 were observed to be coincident with a simultaneous tripping of the counter arrangements. It should be noted that the counter arrangement shown (Fig. 1) was modified during the experiment by increasing the separation of counters. Consideration of the typical arrangement in the diagram shows that a shower of high particle density is necessary to trip

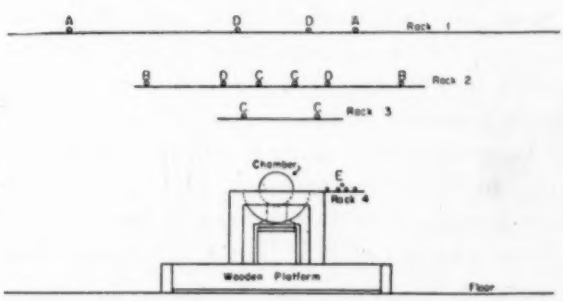

FIG. 1. Arrangement of the ionization chamber and G-M counter sets. The dimensions of the counters in each rack are as follows: Rack 1—2×19 inches; Rack 2—2×15 inches; Rack 3—2×10 inches; Rack 4—1×10 inches.

[1] A. H. Compton, E. O. Wollan, and R. D. Bennett, Rev. Sci. Inst. 5, 415 (1934).

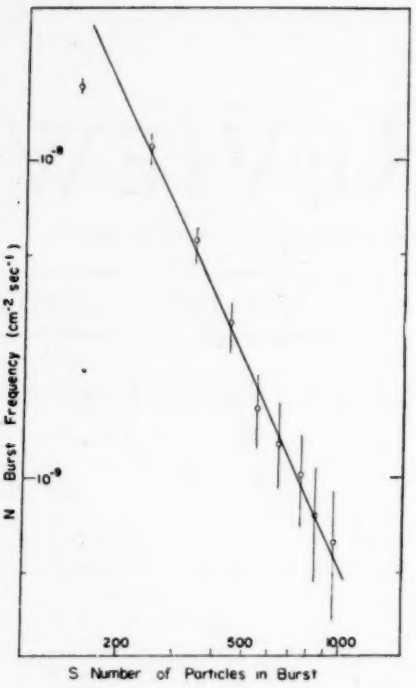

FIG. 2. Cumulative size-frequency distribution curve for bursts observed in an unshielded ionization chamber.

all of the counters. Such showers correspond to those investigated by Auger.[2] Thus the large bursts which occur in an ionization chamber with negligible shower-producing material near it represent a high density region of an Auger shower. Since the Carnegie chamber has an effective area of 0.1 sq. meter, these densities range from 1000 to 30,000 particles per sq. meter. It was observed that some of the Auger showers which tripped all of the counters did not have a sufficient particle density in the region of the ionization chamber to produce a burst in it.

Since the ionization chamber is a unique instrument for the measurement of high particle density in a shower, it is planned to investigate the high density region (the so-called "core") of an Auger shower by using 2 ionization chambers in a coincidence arrangement. Thus it should be possible to measure the extension of the core.

Over a period of 2153 hours, 170 bursts were observed in the chamber. The cumulative[3] size-frequency distribution curve of these bursts (Fig. 2) shows the frequency (N) of bursts containing more than S ionizing particles as a function of S for values of S larger than 100. It is seen that on the double logarithmic plot the experimental points can be approximated by a straight line representing the inverse power law:

$$N(>S)=C\cdot S^{-\gamma},$$

where

$$\gamma=2.15\pm0.35.$$

The apparent discrepancy whereby the smallest size bursts fall out of line with the curve will be discussed in a more general paper on bursts to be published shortly. The problem of bursts under 35 cm of Fe and under intermediate shields of iron around the ionization chamber will also be discussed in the same paper.

From shower theory one can estimate the energy that a primary electron or photon must have in order to initiate at the top of the atmosphere a shower which is able to reach sea level with a high particle density in its core. Thus a burst of 100 particles represents a shower initiated by an electron with energy of about 10^{15} ev. It is estimated that the largest observed burst (3000 particles) must originate from an electron or photon of at least 10^{16}-ev energy. According to the cascade theory of Auger showers, an electron initiates a shower close to the top of the atmosphere; this shower then develops until it has penetrated to sea level, where it extends over at least 10,000 square meters. The frequency of the largest observed bursts (one in 500 hours) as compared with the frequency of Auger showers as measured with counters, shows that the very high density core of the showers has a relatively small area as compared with the total area of the shower. For the largest bursts, the core represents about 1 percent of the total area of the shower.

The writer wishes to thank Dean A. H. Compton for his generous support. The problem was suggested by Professor Marcel Schein, and the writer gratefully acknowledges his continuous advice.

[2] P. Auger, R. Maze, and T. Grivet-Meyer, Comptes rendus 206, 1721 (1938).

[3] M. Schein and P. S. Gill, Rev. Mod. Phys. 11, 267 (1939).

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The Forces Between Hydrogen Molecules

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A quantitative calculation is made of the entire interaction called into play when two hydrogen *molecules* approach. The forces consist of three parts: exchange, quadrupole, and dispersion (van der Waals) forces. By compounding these, it is possible to account in a fundamental way for the size and the shape of the molecules. Also, the interaction curves (Fig. 2) are in reasonable agreement with empirical curves derived from second virial coefficients. Because of the complexity of the exchange force calculation, a simple state function of the Wang type (but with undetermined screening constant) was used in this work to represent the charge distribution within the molecule. Quadrupole moments are computed (Table V), and comments are made on the relation between the molecular problem treated in this paper, and the corresponding atomic problem (interaction between helium atoms).

IN the field of intermolecular forces, interest has chiefly centered about the long range attractive effects which can be calculated with relative ease. Except in the simplest cases of atomic interaction,[1] rather crude devices are in use for estimating the short range forces of repulsion, devices which depend in most instances on empirical knowledge of the gas kinetic sizes of the atoms. For molecules, no attempts have apparently been made to derive the quantitative aspects of the repulsive forces, despite the fact that knowledge of them is indispensable for an adequate understanding of such fundamental properties as molecular size, shape, rigidity. Nor is it possible to determine the position of the van der Waals minimum of the interaction curve without a fairly accurate picture of the repulsive exchange forces.

To obtain these forces without the tedium of an *a priori* calculation, numerous workers[2] have undertaken the useful task of deriving them from observed data, such as second virial coefficients, energies of crystal lattices, Joule-Thomson coefficients, and the like. The relative success of this procedure has created an attitude of satisfaction and apparently a waning of interest in the fundamental problem involved. Endeavor has been shifted toward correlation of diverse gas kinetic phenomena by means of a single set of interaction curves, without much regard to the basic credentials of these curves. The present paper is a step in the opposite direction inasmuch as it derives interaction curves from the elements of quantum mechanics. This may entail a sacrifice in numerical accuracy of the results, but it should fill the gap between semi-empirical reasoning and theoretical understanding.

In the case of molecular hydrogen, the total interaction consists of three main types: First, the exchange forces just mentioned which owe their origin to the interpenetration of the electronic clouds; they are responsible for the rigidity of the molecule. In the calculations they appear as first-order effects, arising when state functions of the proper symmetry are used. They depend very strongly on the relative orientation of the interacting molecules. The major part of this paper is devoted to their study.

Secondly, there are the forces resulting from the presence of a permanent quadrupole moment in the H_2 molecule. Their dependence on orientation is also strong, but they vanish in the mean over all orientations. In comparison with the other types, the quadrupole forces are small except at distances of separation much greater than those of interest in connection with gas-kinetic phenomena. In the calculation, they appear in the same formalism as do the exchange forces, being first-order effects and associated with the symmetry of the molecule. Their

[1] For He, cf. J. C. Slater, Phys. Rev. **32**, 349 (1928); G. Gentile, Zeits. f. Physik **63**, 795 (1930); H. Margenau, Phys. Rev. **56**, 1000 (1939).

[2] Among them are: J. E. Lennard-Jones, Proc. Roy. Soc. **A106**, 463 (1924). For a full review of this work see R. H. Fowler, *Statistical Mechanics*. M. Born and J. E. Mayer, Zeits. f. Physik **75**, 1 (1932). J. O. Hirschfelder, R. B. Ewell, and J. R. Roebuck, J. Chem. Phys. **6**, 205 (1938).

magnitude is a sensitive function of the concentration of electronic charge about the nuclei.

In the third place, the attractive van der Waals forces are to be included.[3] As is well known, they represent the instantaneous attractions between the electronic multipoles as they rotate, within one molecule, in partial phase agreement with the multipoles in the other. These may be calculated by a second-order approximation method and with the use of state functions lacking the correct symmetry. In the H_2 problem, it is necessary to include in the treatment both dipoles and quadrupoles,[3] and it is safe to neglect the interaction of higher multipoles.

I. EXCHANGE FORCES; NOTATION AND METHOD OF CALCULATION

The method used in the calculation of the exchange forces is based on the work of Slater;[4] some of its features, as they relate to the four-electron problem, are discussed by Glasstone, Laidler, and Eyring.[5] In order to achieve simplicity, these authors neglect all multiple exchange effects, thereby reducing the number of exchange integrals from 24 to 7. Unfortunately this curtailment invalidates all quantitative conclusions one might wish to draw, for the exchange integrals do not arrange themselves in descending order of magnitude as the number of transpositions characterizing the exchange increases. They are, in fact, nearly all of comparable magnitude; even if the non-orthogonality between orbitals is small, exchange integrals may well be large. Furthermore, in the case of the hydrogen molecule, the non-orthogonality integral has the value 0.72 and cannot be neglected.

In order to carry through the work, it appears necessary to use the simplest possible type of state function for the H_2 molecule. A function similar to that employed by Wang[6] was therefore chosen. It will be seen, however, that the value of the nuclear charge Z, which gives the lowest energy for a single molecule, leads to erroneous consequences in the present problem. The meaning of this will be discussed in due course; we note at present that this fact enforces the preliminary use of an undetermined Z.

Let the four protons in the two interacting molecules be labeled a, b, c, d. They are first taken to be located at arbitrary, fixed points. The symbols a to d will also be used to represent the hydrogenic wave functions of an electron about the nuclei a to d. Thus, for example,

$$b=(Z^3/\pi a_0^3)^{\frac{1}{2}}\exp(-Zr_b/a_0), \tag{1}$$

r_b denoting the distance of the electron from nucleus b. We note that this function satisfies the Schrödinger equation

$$\left(\frac{\hbar^2}{2m}\nabla^2+\frac{Ze^2}{r_b}\right)b=\tfrac{1}{2}Z^2\frac{e^2}{a_0}\cdot b. \tag{2}$$

The electron coordinates will be numbered from 1 to 4, so that, for instance, $b(3)$ represents electron 3 centered about nucleus b. If the spin functions α, β are introduced in the usual way, a product function like

$$\varphi_1=a(1)\alpha(1)\cdot b(2)\beta(2)\cdot c(3)\alpha(3)\cdot d(4)\beta(4) \tag{3a}$$

signifies a unique assignment of electrons to nuclei. From this product function, an antisymmetric Pauli determinant may be constructed; this, when normalized, will be written in the form:

$$|a\alpha \quad b\beta \quad c\alpha \quad d\beta|. \tag{3}$$

The state of the four atoms under consideration is a singlet state, being composed of two molecules in singlet states. The only functions of type (3) which can cooperate in forming that state are those having a total spin $\Sigma_s=0$, and they are 6 in number:

$$\begin{aligned}
\Psi_1&=|a\alpha \quad b\beta \quad c\alpha \quad d\beta|,\\
\Psi_2&=|a\alpha \quad b\alpha \quad c\beta \quad d\beta|,\\
\Psi_3&=|a\alpha \quad b\beta \quad c\beta \quad d\alpha|,\\
\Psi_4&=|a\beta \quad b\alpha \quad c\alpha \quad d\beta|,\\
\Psi_5&=|a\beta \quad b\alpha \quad c\beta \quad d\alpha|,\\
\Psi_6&=|a\beta \quad b\beta \quad c\alpha \quad d\alpha|.
\end{aligned} \tag{4}$$

[3] For a review of the theory of these forces see H. Margenau, Rev. Mod. Phys. **11**, 1 (1939). Further calculations dealing specifically with H_2 were made by H. S. W. Massey and R. Buckingham, Proc. Ir. Acad. **45**, 31 (1938). See Sec. V of the present paper.

[4] J. C. Slater, Phys. Rev. **38**, 1109 (1931).

[5] S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill, 1941).

[6] S. C. Wang, Phys. Rev. **31**, 579 (1928).

TABLE I. List of symbols used for (1) $\int(P_k\varphi_1)H\varphi_1 d\tau$ and (2) $\int(P_k\varphi_1)\varphi_1 d\tau$. Symbol for integral is given opposite the permutation P_k (which is written in the form of cycles). Unprimed symbols refer to (1), primed symbols to (2).

$(a)(b)(c)(d)$	ϵ, ϵ'	(ab)	u_1, u_1'	(abc)	v_1, v_1'	$(ab)(cd)$	w_1, w_1'	$(abcd)$	z_1, z_1'
		(ac)	u_2, u_2'	(bac)	v_1, v_1'	$(ac)(bd)$	w_2, w_2'	$(dcba)$	z_1, z_1'
		(ad)	u_3, u_3'	(abd)	v_2, v_2'	$(ad)(bc)$	w_3, w_3'	$(bacd)$	z_2, z_2'
		(bc)	u_4, u_4'	(bad)	v_2, v_2'			$(abdc)$	z_2, z_2'
		(bd)	u_5, u_5'	(acd)	v_3, v_3'			$(acbd)$	z_3, z_3'
		(cd)	u_6, u_6'	(cad)	v_3, v_3'			$(dbca)$	z_3, z_3'
				(bcd)	v_4, v_4'				
				(cbd)	v_4, v_4'				

Of these, two singlet functions can be constructed by known rules:[7]

$$\Psi_A=\tfrac{1}{2}(\Psi_1-\Psi_3-\Psi_4+\Psi_5),$$
$$\Psi_B=\tfrac{1}{2}(\Psi_2-\Psi_3-\Psi_4+\Psi_6). \tag{5}$$

Between Ψ_A and Ψ_B the Hamiltonian is to be diagonalized, and this process leads to the secular equation

$$\begin{vmatrix} H_{AA}-E\Delta_{AA} & H_{AB}-E\Delta_{AB} \\ H_{AB}-E\Delta_{AB} & H_{BB}-E\Delta_{BB} \end{vmatrix}=0. \tag{6}$$

When the matrix elements appearing in this equation are expanded with the use of (5), each of them becomes a linear combination of elements H_{ij} and Δ_{ij}, respectively, where the subscripts i, j refer to the set of functions (4). The evaluation of H_{ij} and Δ_{ij} proceeds as follows.

From the properties of the antisymmetric functions and the symmetry of H it is clear that

$$H_{ij}=4!\sum_\mu(-1)^{p_\mu}\int\varphi_i H P_\mu\varphi_j d\tau, \tag{7}$$

where P_μ is some permutation among the four electrons whose coordinates are contained in φ_j, and p_μ is 1 for odd, 2 for even permutations. Also, φ_i is written for the simple product function of type (3a) corresponding to the ψ_i of type (3), and the integral includes summation over the spins. But an integral like $\int\varphi_i H P_\mu\varphi_j d\tau$ can always be reduced to the form

$$\int P_k\varphi_1 H\varphi_1 d\tau$$

with φ_1 given by (3a). We see, therefore, that every H_{ij} is a simple sum of several exchange integrals of this form. These fall, of course, into 5 classes, in accordance with the properties of the symmetric group on four particles. It is well to enumerate and label them by reference to the permutation P_k characterizing the particular integral in question.

In doing so, however, the spin functions may be omitted from φ_1, for they either disappear in the summation or cause the particular integral to vanish. Thus, for example, we shall mean henceforth by

$$\int P_k\varphi_1 H\varphi_1 d\tau$$

simply:

$$\int P_k[a(1)b(2)c(3)d(4)]\times Ha(1)b(2)c(3)d(4)d\tau_1 d\tau_2 d\tau_3 d\tau_4,$$

so that when P_k is (abc), for example,

$$\int P_k\varphi_1 H\varphi_1 d\tau=\int bcadHabcd\cdot d\tau.$$

In Table I we list the names which will be given to the integrals $\int P_k\varphi_1 H\varphi_1 d\tau$ opposite the P_k themselves; the latter are written in the form of cycles.

The equality among some of the integrals is due to the Hermitian character of the Hamiltonian; this causes integrals belonging to a permutation and to its reciprocal to be equal. No further equalities exist unless the position of the nuclei possesses some symmetry, but this cannot be assumed as yet.

The decomposition of H_{ij} into exchange integrals is effected by the use of formula (7); many

[7] See, for example, reference 5.

TABLE II. Matrix elements H_{ij} in terms of exchange integrals.

1	$\epsilon-u_2-u_5+w_2$	$-u_4+v_1+v_4-z_2$	$-u_6+v_4+v_3-z_3$	$-u_1+v_1+v_2-z_3$	$w_1-2z_1+w_3$	$-u_3+v_2+v_3-z_2$
2		$\epsilon-u_1-u_6+w_1$	$-u_5+v_2+v_4-z_1$	$-u_2+v_1+v_3-z_1$	$-u_3+v_3+v_2-z_2$	$w_2-2z_3+w_3$
3			$\epsilon-u_3-u_4+w_3$	$w_1+w_2-2z_2$	$-u_1+v_2+v_1-z_3$	$-u_2+v_1+v_3-z_1$
4				$\epsilon-u_3-u_4+w_3$	$-u_6+v_4+v_3-z_3$	$-u_5+v_2+v_4-z_1$
5					$\epsilon-u_2-u_5+w_2$	$-u_4+v_1+v_4-z_2$
6						$\epsilon-u_1-u_6+w_1$

permutations are absent from the sum because of the orthogonality of the spin functions. In Table II all elements $H_{ij}(=H_{ji})$ are collected.

When the matrix elements H_{AA}, H_{AB}, H_{BB}, which enter into the secular equation, are evaluated by means of Table II, the subsequent expressions result.

$$\begin{aligned}
H_{AA}&=\epsilon+u_1+u_6-\tfrac{1}{2}(u_2+u_3+u_4+u_5)\\
&\quad-(v_1+v_2+v_3+v_4)+w_1+w_2\\
&\quad+w_3-(z_1+z_2-2z_3),\\
H_{BB}&=\epsilon+u_2+u_5-\tfrac{1}{2}(u_1+u_3+u_4+u_6)\\
&\quad-(v_1+v_2+v_3+v_4)+w_1+w_2\\
&\quad+w_3-(z_2+z_3-2z_1),\\
2H_{AB}&=\epsilon+u_1+u_2+u_5+u_6-2u_3-2u_4\\
&\quad-(v_1+v_2+v_3+v_4)+w_1+w_2\\
&\quad+w_3+2(z_1+z_3-2z_2).
\end{aligned}\tag{8}$$

Attention must also be given to Δ_{AA}, Δ_{AB}, and Δ_{BB}. But these are simply related to the corresponding H elements. If we define quantities ϵ', u_i', v_i', w_i', z_i' to be identical with the unprimed quantities given in Table I except that the operator H in the exchange integral is omitted, then the Δ elements result from the H elements on priming all quantities on the right of Eqs. (8).

To proceed further, it is expedient to adopt some conventions regarding the detailed treatment of the Hamiltonian operator in the four-electron problem.

In writing the Hamiltonian we use the following notation: Let r_{ai} be the scalar distance between the ith electron and nucleus a, and put

$$e^2/r_{ai}=\alpha_i,\quad e^2/r_{bi}=\beta_i \text{ etc.};\quad e^2/r_{ij}=\rho_{ij}. \tag{9}$$

Then

$$H=-\frac{\hbar^2}{2m}\sum_1^4\nabla_i^2-\sum_1^4(\alpha_i+\beta_i+\gamma_i+\delta_i)+\sum_{i>j}\rho_{ij}+E_N,$$

provided E_N stands for the repulsive Coulomb energy between the four nuclei. With the use of Eqs. (1) and (2) we now obtain

$$\begin{aligned}
Ha(1)b(2)c(3)d(4)=\Big\{&-2\frac{Z^2e^2}{a_0}\\
&-(1-Z)(\alpha_1+\beta_2+\gamma_3+\delta_4)-(\alpha_2+\alpha_3+\alpha_4\\
&+\beta_1+\beta_3+\beta_4+\gamma_1+\gamma_2+\gamma_4+\delta_1+\delta_2+\delta_3)\\
&+\sum_{i>j}\rho_{ij}+E_N\Big\}a(1)b(2)c(3)d(4).
\end{aligned}\tag{10}$$

II. EXCHANGE INTEGRALS

The exchange integrals ϵ, $u_1\cdots z_3$ listed in Table I may be decomposed into *elementary* exchange integrals, which will now be considered. While in the former the integrand is the entire Hamiltonian (10), the latter contain only one of its terms. To label them both succinctly and naturally, it is expedient to use the abbreviations (9). Thus we shall define

$$(a\gamma d)\equiv\int a(1)\frac{e^2}{r_{c1}}d(1)d\tau_1,$$

$$(ab\rho cd)\equiv\int a(1)b(2)\frac{e^2}{r_{12}}c(1)d(2)d\tau_1d\tau_2,$$

$$\Delta_{ab}\equiv(a\,|\,b)=\int a(1)b(1)d\tau_1,$$

and others in a similar manner. As to symmetry, it will be noted that

$$(a\gamma d)=(d\gamma a),$$
$$(a\alpha b)=(a\beta b),$$
$$(ab\rho cd)=(cb\rho ad)=(ad\rho cb)=(cd\rho ab)=(ba\rho dc).$$

That is to say, the order of the Roman letters on one side of the Greek letter may not be changed if that on the other remains unaltered, but a Roman letter may be shifted freely from one side of the Greek letter to the other, provided its order is unchanged.

The elementary exchange integrals fall into four categories, in accordance with the number of nuclei whose positions affect their value. All *one*-center integrals, like $(a\alpha a)$, $(b\beta b)$ etc., are of course equal and independent of the position of the nuclei. Among the *two*-center integrals one may distinguish four different types, exemplified by the following specimens:

$$(a\beta a),\quad (a\beta b),\quad (ab\rho ab),\quad (ab\rho ba).$$

These all occur in the problem of the hydrogen molecule and are well known.

Three-center integrals fall into three classes, characterized by

$$(a\beta c),\quad (ac\rho bc),\quad (ac\rho cb).$$

For special positions of the nuclei, they have been calculated by Gordadse,[8] Hirschfelder, Eyring, and Rosen,[9] and by Coulson.[10] Since they are of rather complicated structure and, in their exact forms, quite unsuggestive, it is important to have a quick way of estimating their magnitude. Consider, for example, $(a\beta c)$. The product function $a(1)c(1)$ is largest in the region halfway between the nuclei a and c; therefore, if b is far from a and c,

$$(a\beta c)\approx\Delta_{ac}e^2/R_{b,\,ac},$$

where $R_{b,\,ac}$ is the distance from b to the midpoint between a and c. In a similar way,

$$\begin{aligned}(ac\rho bc)&\approx(a\gamma b)\approx\Delta_{ab}e^2/R_{c,\,ab},\\ (ac\rho cb)&\approx\Delta_{ac}\Delta_{bc}e^2/R_{ac,\,bc}.\end{aligned}\tag{11}$$

These approximations are quite accurate when the distances R involved in the formulas are several times as large as the arguments of the Δ functions. The integrals do not, however, become infinite as $R\to 0$; they take simple limiting forms which are either two-center integrals or else very manageable expressions easily obtainable from references 8 and 9.

For more accurate work, approximation (11) is not adequate. On the other hand, the general forms of $(ac\rho bc)$ and $(ac\rho cb)$ which are needed in this work are not known. Their exact calculation would seem to entail rather formidable labor. Fortunately, however, it is possible to avoid most of it by a simple reduction process now to be described.

If the function c^2 is contracted more and more about its nucleus, until finally it becomes a δ function located at the nucleus, the integral $(ac\rho bc)$ turns into $(a\gamma b)$. Alternately, if the function ab is approximated by a δ function located midway between nuclei a and b, the same integral reduces to the two-center integral[11] $(c\overline{\alpha\beta}c)\cdot\Delta_{ab}$. When one distance is larger than the others—as is true in the interaction of two molecules—these reductions can always be made and lead to nearly equal numerical results. This we regard as a test of the validity of the reductions, and we take

$$(ac\rho bc)\cong\tfrac{1}{2}[(a\gamma b)+\Delta_{ab}(c\overline{\alpha\beta}c)].$$

Similar reasoning shows that

$$(ac\rho cb)\cong\tfrac{1}{2}[\Delta_{ac}(c\overline{\alpha\gamma}b)+\Delta_{ab}(a\overline{\gamma\beta}c)].$$

[8] G. S. Gordadse, Zeits. f. Physik **96**, 542 (1935).
[9] J. Hirschfelder, H. Eyring, and N. Rosen, J. Chem. Phys. **4**, 121 (1936).
[10] C. A. Coulson, Proc. Camb. Phil. Soc. **33**, 104 (1937).
[11] $\overline{\alpha\beta}$ here stands for the reciprocal of the electron distance from the midpoint between a and b.

The remaining integrals are known.[9] To give an example of the extent to which this procedure is reliable we consider the case in which the nuclei a, b, c are collinear, c is between a and b and the distance c–b is three times the distance c–b, the latter being the internuclear distance in H_2. The two terms in the above expansion of $(ac\rho cb)$ then have the values 0.1448 and 0.1417 atomic unit, respectively. For larger distances c–b, the reduction works still better.

All *four*-center exchange integrals are of the form $(ab\rho cd)$. Their exact calculation would be extremely tedious if it can be carried out at all. But here again the scheme just described will be used. The reduction can be effected in two ways, and if the results do not differ beyond the tolerated limit of error, their mean is taken as the value of the four-center integral. Thus

$$(ab\rho cd) \approx \tfrac{1}{2}[\Delta_{ac}(b\overline{\alpha\gamma}d)+\Delta_{bd}(a\overline{\beta\delta}c)].$$

When a and c belong to the same molecule, the two terms on the right become very nearly equal, and each approaches $\Delta_R{}^2(e^2/R)$ in the limit in which R, the distance between molecular centers, is large.

We do not wish to lengthen the present paper by an inclusion of the detailed formulas for the residual integrals, which may, if they are found useful in other molecular problems, form the substance of a later communication. As far as our present purposes are concerned, the reader will be relieved to know that an even simpler scheme than the alternate reductions here studied, a scheme which will be described in a later section, leads to significant results for the interaction energy of molecular hydrogen.

When the exchange integrals ϵ, $u_1\cdots z_3$ are expressed in terms of their elements, certain combinations often occur. These will first be singled out. We define

$$\begin{aligned}
A &= (a\alpha a) = Ze^2/a_0,\\
D &= -\tfrac{1}{2}Z^2e^2/a_0,\\
B_{ab} &= e^2/R_{ab}-(a\beta a),\\
C_{ab} &= e^2/R_{ab}+(ab\rho ab)-2(a\beta a),\\
T_{ab} &= (a\beta b)/\Delta_{ab},\\
X_{ab} &= e^2/R_{ab}+(ab\rho ba)/\Delta_{ab}^2-2T_{ab}.
\end{aligned} \tag{12}$$

Here C_{ab} will be recognized as the "Coulomb energy," X_{ab} as the "exchange energy" between two hydrogenic atoms at a and b. All these expressions are functions of only R_{ab}, the distance between a and b, and most of them vanish exponentially at large distances. In addition we need the following more complicated combinations:

$$\begin{aligned}
X'_{ab} &= 2[(ac\rho bc)+(ad\rho bd)-(a\gamma b)-(a\delta b)]/\Delta_{ab},\\
U_{abc} &= \frac{e^2}{R_{ab}}+\frac{e^2}{R_{ac}}+\frac{e^2}{R_{bc}}-(b\alpha c)/\Delta_{bc}-(a\beta c)/\Delta_{ac}-(a\gamma b)/\Delta_{ab}\\
&\qquad +(ab\rho bc)/\Delta_{ab}\Delta_{bc}+(ac\rho ba)/\Delta_{ab}\Delta_{ac}+(bc\rho ca)/\Delta_{bc}\Delta_{ac},\\
U'_{abc} &= \frac{(ad\rho bd)-(a\delta b)}{\Delta_{ab}}+\frac{(bd\rho cd)-(b\delta c)}{\Delta_{bc}}+\frac{(ad\rho cd)-(a\delta c)}{\Delta_{ac}},\\
V_{ab,cd} &= \frac{e^2}{R_{ac}}+\frac{e^2}{R_{ad}}+\frac{e^2}{R_{bc}}+\frac{e^2}{R_{bd}}+4\frac{(ac\rho bd)}{\Delta_{ab}\Delta_{cd}}-2[(a\gamma b)+(a\delta b)]/\Delta_{ab}-2[(c\alpha d)+(c\beta d)]/\Delta_{cd},\\
W_{abcd} &= E_N+\frac{(bc\rho ab)}{\Delta_{ab}\Delta_{bc}}+\frac{(bd\rho ac)}{\Delta_{ab}\Delta_{cd}}+\frac{(ba\rho ad)}{\Delta_{ab}\Delta_{ad}}+\frac{(bc\rho cd)}{\Delta_{bc}\Delta_{cd}}+\frac{(ca\rho bd)}{\Delta_{bc}\Delta_{ad}}+\frac{(da\rho cd)}{\Delta_{cd}\Delta_{ad}}\\
&\qquad -[(a\gamma b)+(a\delta b)]/\Delta_{ab}-[(b\alpha c)+(b\delta c)]/\Delta_{bc}-[(c\alpha d)+(c\beta d)]/\Delta_{cd}-[(a\beta d)+(a\gamma d)]/\Delta_{ad}.
\end{aligned} \tag{13}$$

By permutation of subscripts, other functions can be constructed from this list. Not all of these are different; for instance it will be seen on inspection that there are four different U functions (U_{abc}, U_{abd}, U_{acd}, U_{bcd}), three different V functions ($V_{ab,cd}$, $V_{ac,bd}$, $V_{ad,bc}$), and three different W functions (W_{abcd}, W_{bacd}, W_{acbd}). Only X' and U' have the property of vanishing when a reduction of the type (11) is performed, which may be taken as an indication that they are generally small. They disappear when the nuclei in each molecule coalesce.

The function $V_{ab,cd}$ has a rather interesting significance. When it is "reduced," it represents the electrostatic interaction between two linear quadrupoles, one consisting of protons at a and b with two electrons at the midpoint between them, the other of protons at c and d and two electrons at their midpoint. We shall show later that this is indeed its true significance, and that the value of this integral is well approximated by this quadrupole interaction.

With the use of these abbreviations, the exchange integrals take on symmetrical—even if somewhat complicated—forms, *viz.*:

$$\epsilon = 4D + 4(Z-1)A + C_{ab} + C_{ac} + C_{ad} + C_{bc} + C_{bd} + C_{cd},$$

$$\begin{aligned}
u_1 &= \Delta_{ab}^2[4D + 2(Z-1)(A+T_{ab}) + X_{ab} + B_{ac} + B_{ad} + B_{bc} + B_{bd} + C_{cd} + X'_{ab}],\\
u_2 &= \Delta_{ac}^2[4D + 2(Z-1)(A+T_{ac}) + X_{ac} + B_{ab} + B_{ad} + B_{bc} + B_{cd} + C_{bd} + X'_{ac}],\\
u_3 &= \Delta_{ad}^2[4D + 2(Z-1)(A+T_{ad}) + X_{ad} + B_{ab} + B_{ac} + B_{bd} + B_{cd} + C_{bc} + X'_{ad}],\\
u_4 &= \Delta_{bc}^2[4D + 2(Z-1)(A+T_{bc}) + X_{bc} + B_{ab} + B_{ac} + B_{bd} + B_{cd} + C_{ad} + X'_{bc}],\\
u_5 &= \Delta_{bd}^2[4D + 2(Z-1)(A+T_{bd}) + X_{bd} + B_{ab} + B_{ad} + B_{bc} + B_{cd} + C_{ac} + X'_{bd}],\\
u_6 &= \Delta_{cd}^2[4D + 2(Z-1)(A+T_{cd}) + X_{cd} + B_{ac} + B_{ad} + B_{bc} + B_{bd} + C_{ab} + X'_{cd}],
\end{aligned}$$

$$\begin{aligned}
v_1 &= \Delta_{ab}\Delta_{ac}\Delta_{bc}[4D + B_{ad} + B_{bd} + B_{cd} - (2-Z)(T_{ab} + T_{ac} + T_{bc}) + (Z-1)A + U_{abc} + U'_{abc}],\\
v_2 &= \Delta_{ab}\Delta_{bd}\Delta_{ad}[4D + B_{ac} + B_{bc} + B_{cd} - (2-Z)(T_{ab} + T_{bd} + T_{ad}) + (Z-1)A + U_{abd} + U'_{abd}],\\
v_3 &= \Delta_{ac}\Delta_{cd}\Delta_{ad}[4D + B_{ab} + B_{bc} + B_{bd} - (2-Z)(T_{ac} + T_{cd} + T_{ad}) + (Z-1)A + U_{acd} + U'_{acd}],\\
v_4 &= \Delta_{bc}\Delta_{cd}\Delta_{bd}[4D + B_{ab} + B_{ac} + B_{ad} - (2-Z)(T_{bc} + T_{cd} + T_{bd}) + (Z-1)A + U_{bcd} + U'_{bcd}],
\end{aligned} \tag{14}$$

$$\begin{aligned}
w_1 &= \Delta_{ab}^2\Delta_{cd}^2[4D + X_{ab} + X_{cd} + 2(Z-1)(T_{ab} + T_{cd}) + V_{ab,cd}],\\
w_2 &= \Delta_{ac}^2\Delta_{bd}^2[4D + X_{ac} + X_{bd} + 2(Z-1)(T_{ac} + T_{bd}) + V_{ac,bd}],\\
w_3 &= \Delta_{ad}^2\Delta_{bc}^2[4D + X_{ad} + X_{bc} + 2(Z-1)(T_{ad} + T_{bc}) + V_{ad,bc}],
\end{aligned}$$

$$\begin{aligned}
z_1 &= \Delta_{ab}\Delta_{bc}\Delta_{cd}\Delta_{ad}[4D - (2-Z)(T_{ab} + T_{bc} + T_{cd} + T_{ad}) + W_{abcd}],\\
z_2 &= \Delta_{ac}\Delta_{ab}\Delta_{cd}\Delta_{bd}[4D - (2-Z)(T_{ac} + T_{ab} + T_{cd} + T_{bd}) + W_{bacd}],\\
z_3 &= \Delta_{ac}\Delta_{bd}\Delta_{bc}\Delta_{ad}[4D - (2-Z)(T_{ac} + T_{bd} + T_{bc} + T_{ad}) + W_{acbd}].
\end{aligned}$$

Thus far our development has been quite general. We can now afford to make specific assumptions: Protons a and b belong to one molecule, protons c and d to the other; the distances a–b and c–d are equal. Functions with subscripts ab and cd may therefore be written without subscripts, the understanding being that they are to be evaluated for the internuclear distance of the H_2 molecule. It is also possible to distinguish different orders of magnitude among the various constituents of Eqs. (14). All quantities without subscripts (or with subscripts ab, cd) are large, all others small. Whether a term can be totally neglected can only be decided by inspection of the Δ functions which multiply it. This overlap integral has the well-known simple form

$$\Delta_{ab} = \Delta(s) = (1 + s + \tfrac{1}{3}s^2)e^{-s},$$

s being $(Z/a_0)R_{ab}$. The ratio Δ_{ac}/Δ_{ab} is therefore always fairly small, and it is safe to neglect its

fourth power, though not the second. We are thus enabled to simplify the list (14) somewhat, as follows:

$$\epsilon = 4D+4(Z-1)A+2C+C_{ac}+C_{ad}+C_{bc}+C_{bd},$$

$$\begin{aligned}
u_1 &= \Delta^2[4D+X+C+2(Z-1)(A+T)+B_{ac}+B_{ad}+B_{bc}+B_{bd}],\\
u_2 &= \Delta_{ac}^2[4D+2B+2(Z-1)A+X_{ac}+X'_{ac}+2(Z-1)T_{ac}],\\
u_3 &= \Delta_{ad}^2[4D+2B+2(Z-1)A+X_{ad}+X'_{ad}+2(Z-1)T_{ad}],\\
u_4 &= \Delta_{bc}^2[4D+2B+2(Z-1)A+X_{bc}+X'_{bc}+2(Z-1)T_{bc}],\\
u_5 &= \Delta_{bd}^2[4D+2B+2(Z-1)A+X_{bd}+X'_{bd}+2(Z-1)T_{bd}],\\
u_6 &= u_1,
\end{aligned}$$

$$\begin{aligned}
v_1 &= \Delta\Delta_{ac}\Delta_{bc}[4D+B-(2-Z)T+(Z-1)A+U_{abc}+U'_{abc}-(2-Z)(T_{ac}+T_{bc})],\\
v_2 &= \Delta\Delta_{bd}\Delta_{ad}[4D+B-(2-Z)T+(Z-1)A+U_{abd}+U'_{abd}-(2-Z)(T_{bd}+T_{ad})],\\
v_3 &= \Delta\Delta_{ac}\Delta_{ad}[4D+B-(2-Z)T+(Z-1)A+U_{acd}+U'_{acd}-(2-Z)(T_{ac}+T_{ad})],\\
v_4 &= \Delta\Delta_{bc}\Delta_{bd}[4D+B-(2-Z)T+(Z-1)A+U_{bcd}+U'_{bcd}-(2-Z)(T_{bc}+T_{bd})],
\end{aligned} \tag{14b}$$

$$\begin{aligned}
w_1 &= \Delta^4[4D+2X+4(Z-1)T+V_{ab,cd}],\\
w_2 &= w_3 = 0,
\end{aligned}$$

$$\begin{aligned}
z_1 &= \Delta^2\Delta_{bc}\Delta_{ad}[4D-2(2-Z)T-(2-Z)(T_{bc}+T_{ad})+W_{abcd}],\\
z_2 &= \Delta^2\Delta_{ac}\Delta_{bd}[4D-2(2-Z)T-(2-Z)(T_{ac}+T_{bd})+W_{bacd}],\\
z_3 &= 0.
\end{aligned}$$

In u_1 the term X' has been dropped because of its smallness, and in u_2 to u_5, the C functions are neglected. Numerical comparison with terms retained will justify this curtailment.

The primed functions, defined in Table I, are easily obtained from this list; for they are simply the product of Δ functions which appears in the equations for their unprimed mates. Thus, for example, $\epsilon' = 1$, $u_1' = \Delta^2$, $v_4 = \Delta\Delta_{bc}\Delta_{bd}$ etc. We are now ready to compute the two roots E of Eq. (6).

III. GENERAL EXPRESSION FOR EXCHANGE ENERGY

Of the two solutions of the determinantal Eq. (6), the one of interest is that which will represent the energy of two H_2 molecules at infinite internuclear distance. It is convenient, therefore, to solve the equation first of all "in zeroth order," i.e., with the neglect of all terms which vanish at infinite separation.

As a preliminary, let us recall the results of the Heitler-London treatment of the single molecule and translate them into the present notation. Here we have

$$\psi_1 = |a\alpha \quad b\beta|, \quad \psi_2 = |a\beta \quad b\alpha|,$$

and $\psi_\pm = \psi_1 \pm \psi_2$. The function ψ_+ represents the triplet, ψ_- the singlet or normal state of the molecule. In view of Eqs. (2) and (12)

$$Hab = [2D+(Z-1)(\alpha_1+\beta_2)-\alpha_2-\beta_1+\rho_{12}+e^2/R_{ab}]ab$$

so that

$$\int \psi_\pm H \psi_\pm d\tau = 2\{2D+C+2(Z-1)A \mp [2D+2(Z-1)T+X]\Delta^2\}$$

whereas

$$\int \psi_\pm^2 d\tau = 2[1 \mp \Delta^2].$$

For the ratio of these, which represents the energy of the molecule, we have

$$E(H_2)=2D+(1\mp\Delta^2)^{-1}\{C+2(Z-1)A\mp\Delta^2[X+2(Z-1)T]\}, \tag{15}$$

where the *lower* signs refer to the stable state. The second part of this expression represents the molecular energy since $2D$ is the energy of two hydrogen atoms of nuclear charge Ze (cf. Eq. (12)). Wang has found the value of Z which minimizes (15) to be 1.166.

We now turn to Eq. (6), in which the H elements must be expressed in terms of the functions (12) and (13) via Eqs. (8) and (14). Before doing this it is well to note the effect of subtracting $E\Delta_{AA}$ from H_{AA}. From what has been said about the Δ elements it is apparent that this subtraction merely amounts to the replacement, in H_{AA}, of every term $4D$ by $4D-E$. The same is true regarding $H_{AB}-E\Delta_{AB}$ and $H_{BB}-E\Delta_{BB}$. We therefore define new matrix elements, K_{AA}, K_{AB}, K_{BB}, which differ from the corresponding components of H merely in the substitution of

$$-E'\equiv 4D-E$$

for $4D$. According to its definition, E' is the total molecular energy of the two interacting partners, including the binding energy of each molecule. Equation (6) now reads

$$\begin{vmatrix} K_{AA} & K_{AB} \\ K_{AB} & K_{BB} \end{vmatrix}=0. \tag{16}$$

In zeroth approximation, only those parts of (14b) need be retained which bear no subscripts. This leaves us only with parts of ϵ, u_1, u_6, and w_1. When these are used in (8), we find

$$\begin{aligned} K^0_{AA}&=-E'+2C+4(Z-1)A+2\Delta^2[-E'+X+C+2(Z-1)(A+T)]+\Delta^4[-E'+2X+4(Z-1)T], \\ K^0_{BB}&=-E'+2C+4(Z-1)A-\Delta^2[-E'+X+C+2(Z-1)(A+T)]+\Delta^4[-E'+2X+4(Z-1)T], \\ K^0_{AB}&=\tfrac{1}{2}K^0_{AA}. \end{aligned} \tag{17}$$

On insertion of these expressions into (16) there results

$$K^0_{AA}(K^0_{BB}-\tfrac{1}{4}K^0_{AA})=0,$$

and this allows the two roots to be determined by putting

$$K^0_{AA}=0 \quad \text{and} \quad K^0_{BB}=\tfrac{1}{4}K^0_{AA}.$$

When these are solved for E', the first leads to $2E(H_2)$ as given by Eq. (15) with the choice of the positive signs, the second to the same equation, but with negative signs. Our interest is therefore confined to that root of Eq. (16) which is given in zeroth approximation by the equation

$$K^0_{AA}=0. \tag{18}$$

We now show that the interaction energy which is being sought is similarly a solution of

$$K_{AA}=0 \tag{19}$$

so that we need not calculate the elements K_{BB} and K_{AB} at all for the purposes of the present problem.

Let us put

$$K_{AA}=-LE'+L_0+lE'+l_0$$

where $-LE'+L_0$ represents K^0_{AA} (the coefficients L and L_0 are easily identifiable from (17)), the remainder being small. We may then treat L and L_0 as "large," l and l_0 as small coefficients. Similarly

$$K_{AB}=-ME'+M_0+mE'+m_0$$

and we know from (17) that $M=\frac{1}{2}L$, $M_0=\frac{1}{2}L_0$. Finally,

$$K_{BB}=-NE'+N_0+nE'+n_0.$$

In solving (16), it is now convenient to write

$$E' = E_0' + \eta,$$

E_0' being the solution of (18), i.e. the energy of the two H_2 molecules at infinite separation. The determinant (16) then reads

$$\begin{vmatrix} -LE_0'+L_0-L\eta+lE_0'+l_0 & -ME_0'+M_0-M\eta+mE_0'+m_0 \\ -ME_0'+M_0-M\eta+mE_0'+m_0 & -NE_0'+N_0-N\eta+nE_0'+n_0 \end{vmatrix} = 0.$$

In expanding it, the squares of small terms may be omitted, and we know that only the first two summands of each element are large. Also, $E_0' = L_0/L$. Insertion of this causes all large terms in the elements of the first row to disappear because $L/L_0 = M/M_0$. Expansion then gives

$$\eta = L^{-1}(lE_0' + l_0), \tag{20}$$

and this is simply the condition (19). We turn, therefore, to the evaluation of K_{AA}. When the terms are suitably grouped, there results

$$\begin{aligned} K_{AA} = &-(1+\Delta^2)^2\eta + [\tfrac{1}{2}E_0' - B - (Z-1)A](\Delta_{ac}^2 + \Delta_{ad}^2 + \Delta_{bc}^2 + \Delta_{bd}^2) \\ &+ C_{ac} + C_{ad} + C_{bc} + C_{bd} + 2\Delta^2(B_{ac} + B_{ad} + B_{bc} + B_{bd}) - \tfrac{1}{2}\Delta_{ac}^2[X_{ac} + X'_{ac} + 2(Z-1)T_{ac}] \\ &- \tfrac{1}{2}\Delta_{ad}^2[X_{ad} + X'_{ad} + 2(Z-1)T_{ad}] - \tfrac{1}{2}\Delta_{bc}^2[X_{bc} + X'_{bc} + 2(Z-1)T_{bc}] \\ &- \tfrac{1}{2}\Delta_{bd}^2[X_{bd} + X'_{bd} + 2(Z-1)T_{bd}] + \Delta(\Delta_{ac}\Delta_{bc} + \Delta_{ad}\Delta_{bd} + \Delta_{ac}\Delta_{ad} + \Delta_{bc}\Delta_{bd}) \\ &\times [E_0' - B - (Z-1)A + (2-Z)T] - \Delta\Delta_{ac}\Delta_{bc}[U_{abc} + U'_{abc} - (2-Z)(T_{ac} + T_{bc})] \\ &- \Delta\Delta_{ad}\Delta_{bd}[U_{abd} + U'_{abd} - (2-Z)(T_{ad} + T_{bd})] - \Delta\Delta_{ac}\Delta_{ad}[U_{acd} + U'_{acd} - (2-Z)(T_{ac} + T_{ad})] \\ &- \Delta\Delta_{bc}\Delta_{bd}[U_{bcd} + U'_{bcd} - (2-Z)(T_{bc} + T_{bd})] + \Delta^2(\Delta_{bc}\Delta_{ad} + \Delta_{ac}\Delta_{bd})[E_0' + 2(2-Z)T] \\ &- \Delta^2\Delta_{bc}\Delta_{ad}[W_{abcd} - (2-Z)(T_{bc} + T_{ad})] - \Delta^2\Delta_{ac}\Delta_{bd}[W_{bacd} - (2-Z)(T_{ac} + T_{bd})] + \Delta^4 V_{ab,cd}. \end{aligned} \tag{21}$$

η is the exchange energy we are seeking; it is found by equating K_{AA} to zero.

IV. NUMERICAL RESULTS

When preliminary computations based on the use of Eq. (21) were made, a rather curious fact emerged. At first Z was taken to be 1, then 1.166 (Wang's value), and in both cases did η become ***negative*** at all significant distances of interaction. In this work, alternate reductions were made as described earlier, and careful attention was paid to the approximations involved; the conclusion was reached that the negative result was not occasioned by inaccuracies in the numerical evaluation of the integrals. To test the matter further, the integrals constituting η were simplified by allowing the nuclei of each molecule to coalesce. The result was then identical formally with the interaction energy of two helium atoms. In that problem, too, η is negative for $Z=1$ and 1.166. It is possible to show, moreover, that the helium interaction, calculated by means of hydrogenic functions, is repulsive only for values of Z above the critical value $Z=11/8$. Since this appears to be a somewhat interesting feature of the 4-electron interaction, we shall prove it in a later section. For He, of course, the matter is unimportant since the value of Z which minimizes the atomic energy is 27/16, well above the critical value. One would expect, then, that in our problem Z also possesses such a critical value, presumably in the neighborhood of 11/8.

In a sense, this is a rather sad commentary on the adequacy of the Wang function for the purpose at hand,[12] which might induce one to look for better wave functions. The complexity of the present calculation, however, definitely counsels against that undertaking. The situation appears even more embarrassing when it is noted that Wang's value of Z describes the polariza-

[12] A more favorable, literal interpretation of this result would entail the consequence that hydrogen molecules, while indeed attracting each other dynamically at nearly all distances, are kept apart for reasons of entropy. This, however, we do not believe to be the case.

bility of H_2 surprisingly well,[13] gives a good account of its magnetic susceptibility and a reasonable one of the dispersion forces.[14]

But on further reflection, the puzzling aspects fade away. The effective nuclear charge has no definite physical significance—except insofar as it measures roughly the concentration of the electron cloud—and may well take on different values in different physical problems. In particular, there is nothing unique about the Z which minimizes the molecular energy. It happens that in the calculations of the polarizability, the susceptibility, and the dispersion forces the *mean square* of the charge distribution is of importance, and this would account for a common Z. The present problem, however, has altogether different features.

The change in Z from 1 to 1.166 which occurs as we pass from the free hydrogen atom to the molecule is a measure of the increased electron concentration about each proton occurring as a result of the repulsion by the other electron. The term "screening," though quite adequate in atomic problems, loses its significance here. Now, when two molecules interact, there is not only *one* electron which tends to drive a given electron back to its nucleus, but *three*. This crude picture may be made to give a qualitative indication of the value of Z to be chosen in the present problem: If one electron causes an increase in Z from 1 to 1.166, three might increase it from 1 to about 1.5. A similar result could be argued in this way: as the two nuclei of the H_2 molecule coalesce, Z changes from 1 to 2; as the four nuclei here under consideration are made to coalesce, Z changes from 1 to 4 (except for screening, which is neglected in both instances). Wang's value of Z represents a stage in the process of coalescence 1/6 on its way toward completion; the corresponding stage in the four-electron problem is given by $Z=1.5$. This result is likely to be too large, of course, because the distance between nuclei in the different molecules is greater than in H_2.

[13] J. O. Hirschfelder, J. Chem. Phys. **3**, 555 (1935). We have computed the polarizability of H_2 as a function of Z and have found that $Z=1.167$ gives about the best fit with observation.

[14] H. S. W. Massey and R. Buckingham, Proc. Ir. Acad. **45**, 31 (1938).

While we do not wish to ascribe much quantitative significance to the present argument, we are forced, in the absence of more conclusive evidence, to use it. The exchange forces do not depend as sensitively on Z as, for example, the second-order forces. Our results will not be changed decisively by a change in Z from 1.4 to 1.5. In the following we select one approximately "right" value, $Z=1.428$, and one "wrong" value, $Z=1.785$ for comparison. Their exact choice was dictated by numerical convenience; the first makes the parameter Zd/a_0, wherein d is the internuclear distance of H_2, equal to 2, the second to 2.5.

The preliminary calculations further indicate that a certain simplification is permitted. Among the functions occurring in η, there are many which vary slowly as the nuclei of each molecule are made to coalesce. In these we may proceed to the limit in which $R_{ab}=R_{cd}=0$. Then, if we denote the distance between molecular centers by R,

$$\text{all} \quad X' \to 0,$$

$$U' \to 0,$$

$$U_{abc} \to X(R)+B(R)+M(R) - \frac{2e^2}{R}+\frac{e^2}{R_{ac}}+\frac{e^2}{R_{bc}}+\frac{e^2}{d},$$

$$W_{abcd} \to X(R)+2B(R) + C(R)+2M(R)-2T(R) + \frac{2e^2}{d}+\frac{e^2}{R_{ac}}+\frac{e^2}{R_{ad}}+\frac{e^2}{R_{bc}}+\frac{e^2}{R_{bd}}-\frac{4e^2}{R},$$

$$W_{bacd}=W_{abcd}.$$

The other three U functions are formed by fairly obvious permutations of subscripts. The new quantity M which appears here is given by

$$M_{ac}=2(aa\rho ac)/\Delta_{ac}.$$

$M(R)$ may be approximated by either $2T(R)$ or, better, by $T(R)+(2e^2/R)-B(R/2)$. We finally introduce the abbreviations $E(abc)$ for the electrostatic repulsive energy between protons a, b, and c (and similarly $E(abcd)$ for the former E_N),

$$\kappa \equiv Z-1$$

TABLE III. Values of numerical constants used. All energies are stated in units Ze^2/a_0.

Z	1.428	1.785
Zd/a_0	2.0	2.5
Δ	0.5865	0.4583
A	1	1
B	0.0275	0.0094
C	− .0191	− .0128
X	− .349	− .348
T	0.692	0.626
E_0'	1.370	2.794

and obtain from (21)

$$\begin{aligned}\eta=(1+\Delta^2)^{-2}\{&2\Delta^2(B_{ac}+B_{ad}+B_{bc}+B_{bd})\\&+C_{ac}+C_{ad}+C_{bc}+C_{bd}\\&+(\Delta_{ac}^2+\Delta_{ad}^2+\Delta_{bc}^2+\Delta_{bd}^2)(\tfrac{1}{2}E_0'-B-\kappa A)\\&-\tfrac{1}{2}\Delta_{ac}^2(X_{ac}+2\kappa T_{ac})-\tfrac{1}{2}\Delta_{ad}^2(X_{ad}+2\kappa T_{ad})\\&-\tfrac{1}{2}\Delta_{bc}^2(X_{bc}+2\kappa T_{bc})-\tfrac{1}{2}\Delta_{bd}^2(X_{bd}+2\kappa T_{bd})\\&+\Delta(\Delta_{ac}\Delta_{bc}+\Delta_{ad}\Delta_{bd}+\Delta_{ac}\Delta_{ad}+\Delta_{bc}\Delta_{bd})\\&\times[E_0'-B+(1-\kappa)T-\kappa A-X(R)\\&-B(R)-2\kappa T(R)+(2e^2/R)]\\&-\Delta[\Delta_{ac}\Delta_{bc}E(abc)+\Delta_{ad}\Delta_{bd}E(abd)\\&+\Delta_{ac}\Delta_{ad}E(acd)+\Delta_{bc}\Delta_{bd}E(bcd)]\\&+\Delta^2(\Delta_{bc}\Delta_{ad}+\Delta_{ac}\Delta_{bd})\\&\times\Big[E_0'+2(1-\kappa)T-X(R)-2B(R)-C(R)\\&-2\kappa T(R)+\frac{4e^2}{R}-E(abcd)\Big]+\Delta^4V_{ab,\,cd}.\end{aligned}\tag{22}$$

For reference, we recall:

$$E_0'=2\frac{C+\Delta^2X+2\kappa(A+\Delta^2T)}{1+\Delta^2}.$$

The numerical results now to be reported were based on this approximation. Equation (22) is slightly less sensitive to orientation of the molecules than (21), but the economy of labor which it effects recommends its use despite this fault. The values of constants are collected in Table III. From the last entry the *binding energy* of the molecule for the assumed value of Z may be obtained, since, as may easily be verified, it is given by $E_0'Z/2-(Z^2-1)$. This is -1.65 ev for the smaller, $+8.33$ ev for the larger Z. In the latter case, therefore, the hydrogen molecule would not be stable at all.

Three relative orientations of the molecules have been treated. In

Case (a): both molecular axes are parallel to R, the line joining the centers;
Case (b): one axis is parallel, the other is perpendicular to R;
Case (c): both axes are perpendicular to R.

The results for η, exclusive of the term $\Delta^4V_{ab,\,cd}$, are given in Table IV. It is perhaps worth mentioning that in the region here of interest η can be approximated fairly well by an expression of the form

$$\eta=Ae^{-bS}$$

in which b differs but little in all 6 cases, having the value 1.55 ± 0.10, while A varies markedly from instance to instance. The quantity S represents the distance R measured in units a_0/Z.

V. QUADRUPOLE FORCES

We have already interpreted the last term of Eq. (22), $[\Delta^2/(1+\Delta^2)]^2V_{ab,\,cd}$, as the quadrupole energy on the evidence that V "reduces" to the electrostatic interaction between the two structures of Fig. 1 when the approximation (11) is made. In this approximation, then, V is given by the formula[15] appropriate for *linear* quadrupoles,

$$V=\frac{3Q^2}{4R^5}f(\theta_1,\,\theta_2,\,\varphi),\tag{23}$$

in which Q, the quadrupole moment, is $2e^2(d/2)^2$, and f is the function characteristic of this type of interaction. Explicitly, if θ_1 and θ_2 are the angles which the molecular axes make with R, the line between centers, and φ is the difference between azimuths in a plane at right angles to R, then

$$\begin{aligned}f=&1-5\cos^2\theta_1-5\cos^2\theta_2-15\cos^2\theta_1\cos^2\theta_2\\&+2(4\cos\theta_1\cos\theta_2+\sin\theta_1\sin\theta_2\cos\varphi)^2.\end{aligned}\tag{24}$$

Our calculation shows that this interaction between *point* charges must be multiplied by the "diffuseness factor" $[\Delta^2/(1+\Delta^2)]^2$ in order to represent the true interaction between the charge clouds.

The present approximation is in fact suffi-

[15] See review article, reference 3.

ciently good for our purposes, but it is interesting to point out that an accurate calculation merely causes the term Q in (23) to be multiplied by 4/5. A calculation of this kind has already been made by Massey and Buckingham,[14] whose work was limited to one special value of Z. Since their result is written in a rather cumbersome form which veils its simplicity, and our derivation is short, we shall give it here.

Equation (23) is valid in general, provided we replace Q by its quantum mechanical equivalent:

$$Q'=\tfrac{1}{2}\sum_i e_i\langle r_i^2-3z_i^2\rangle_{Av}.$$

Here r_i and z_i refer to the positions of the various charges e_i, and the average is a quantum one. The sum extends over the 4 particles composing the molecule. We take the Z axis along the molecule. The protons will then contribute to this sum the amount $-4e(d/2)^2$. For the electrons, $\langle r_i^2\rangle_{Av}=\langle 2x_i^2\rangle_{Av}+\langle z_i^2\rangle_{Av}$; hence their contribution to the sum is $-4e(\langle x^2\rangle_{Av}-\langle z^2\rangle_{Av})$. The subscript may here be dropped because the electrons are indistinguishable. In view of these simple facts,

$$Q'=-2e\left(\frac{d^2}{4}-\langle z^2\rangle_{Av}+\langle x^2\rangle_{Av}\right).$$

The mean values appearing here are not difficult to calculate when hydrogenic wave functions are used—they also occur in the theory of polarizabilities.[13] In general,

$$\langle z^2\rangle_{Av}=(1+\Delta^2)^{-1}\left[\langle z_0^2\rangle_{Av}+\frac{d^2}{4}+\Delta\int\zeta^2abd\tau\right],$$

TABLE IV. Exchange energy (η) as function of intermolecular separation (R).

S	R (in A)	η (in volts) Pos. a	Pos. b	Pos. c
$Z=1.428$				
6	2.22	0.358	0.249	0.150
7	2.59	0.102	0.0602	0.0344
8	2.96	0.0231	0.0135	0.00744
9	3.33	0.00504	0.00287	0.00153
10	3.70	0.00104	0.000582	0.000302
11	4.07	0.000200	0.000114	0.0000579
$Z=1.785$				
6	1.78	1.390	0.754	0.325
7	2.07	0.426	0.192	0.0764
8	2.37	0.100	0.0449	0.0173
9	2.66	0.0247	0.00986	0.00354
10	2.96	0.00545	0.00205	0.000711
11	3.25	0.00113	0.000451	0.000137

FIG. 1. Molecular structure and arrangement for calculation of electrostatic energy.

$$\langle x^2\rangle_{Av}=(1+\Delta^2)^{-1}\left[\langle x_0^2\rangle_{Av}+\Delta\int\xi^2abd\tau\right].$$

Here $\langle z_0^2\rangle_{Av}=\langle x_0^2\rangle_{Av}$ are averages taken over the electron in the H atom, ξ and ζ are, respectively, the x and z coordinates measured from the *center* of the molecule. For the functions here used,

$$\int\zeta^2abd\tau=\frac{a_0^2}{Z^2}e^{-s}\left(1+s+\frac{9}{20}s^2+\frac{7}{60}s^3+\frac{1}{60}s^4\right),$$

$$\int\xi^2abd\tau=\frac{a_0^2}{Z^2}e^{-s}\left(1+s+\frac{2}{5}s^2+\frac{1}{15}s^3\right),\quad s=\frac{dZ}{a_0}.$$

Remembering the form of Δ (cf. appendix), we find

$$\langle x^2\rangle_{Av}-\langle z^2\rangle_{Av}=-\frac{d^2}{4}(1+\Delta^2/5)\Big/(1+\Delta^2)$$

and finally

$$Q'=-2e\cdot\frac{4}{5}\frac{\Delta^2}{1+\Delta^2}\frac{d^2}{4}. \tag{25}$$

The quadrupole moment depends on Z only through the overlap integral Δ, and in this simple way; the factor $\Delta^2/(1+\Delta^2)$ appears automatically in the calculation, justifying our former remarks. Collecting the results of the present section, we write for the quadrupole energy

$$E_Q=\frac{3}{25}\left(\frac{\Delta^2}{1+\Delta^2}\right)^2\frac{e^2d^4}{R^5}\cdot f(\theta_1,\theta_2,\varphi). \tag{26}$$

The function f (cf. Eq. (24)) causes E_Q to vanish when a mean value is formed over all orientations.

The quadrupole moment is listed as a function of Z in Table V, where $-Q'$ is stated in units ea_0^2. The values of E_Q, given in Table VI for cases (a), (b), and (c), are seen to be small in comparison with the exchange energy in Table IV.

VI. LONG RANGE VAN DER WAALS FORCES

The dipole-dipole part of the long range forces has been calculated for the present problem by Massey and Buckingham using $Z=1.166$. As to the dependence of these forces on orientation, their result indicates a variation of about 50 percent as we pass from case (c) to case (a). The corresponding variation in η is measured by a factor 3. When compounding the various components of the total interaction, we shall therefore permit ourselves to neglect the dependence on orientation of the long range forces.[16] The numerical result for the mean over all orientations given by the aforementioned authors is

$$\bar{E}_{\text{v.d.w}}=-16.0\frac{e^2}{a_0}\left(\frac{a_0}{R}\right)^6; \qquad (27)$$

they also point out that it agrees reasonably well with empirical facts as far as they are available.

In using this result in the present calculation we should be guilty of employing different values of Z in different parts of the problem. As has been noted, there is nothing basically contradictory in such a procedure because a variation in the best choice of Z may well be expected to occur as we pass from one calculation to another. Nevertheless we do not wish to leave this point without further investigation, which will also throw some light on the accuracy of Eq. (27).

In the first place, it is easy to obtain $\bar{E}_{\text{v.d.w}}$ for other values of Z by use of the variation method of reference 14. Taking $Z=1.428$, we find

$$\bar{E}_{\text{v.d.w}}=-5.4\frac{e^2}{a_0}\left(\frac{a_0}{R}\right)^6,$$

which is almost certainly too low. Roughly, the dipole-dipole energy is proportional to Z^{-5}.

Perhaps the most accurate semi-empirical method[3] of computing the term here in question is to employ dispersion f values which, for H_2, are known with considerable accuracy. For this purpose, London's formula may be used:

$$\bar{E}_{\text{v.d.w}}\doteq-\frac{3}{2}\frac{e^4}{m^2}\frac{\hbar^4}{R^6}\sum_{ij}\frac{f_if_j}{\Delta E_i\Delta E_j(\Delta E_i+\Delta E_j)},$$

where the f's are oscillator strengths and the ΔE's the corresponding excitation frequencies. For H_2, Wolf and Herzfeld[17] find that the dispersion curve can be represented with remarkable accuracy by a two-term formula in which

$$f_1=0.69,\quad E_1=2.71\times10^{-11}\text{ erg}=0.630e^2/a_0,$$
$$f_2=0.84,\quad E_2=2.12\times10^{-11}\text{ erg}=0.492e^2/a_0.$$

These data yield

$$\bar{E}_{\text{v.d.w}}=-10.9\frac{e^2}{a_0}\left(\frac{a_0}{R}\right)^6 \qquad (28)$$

in place of (27). This, incidentally, confirms the author's former conjecture that the variational Hassé method, employed by Massey and Buckingham, usually gives too large an answer for the van der Waals force. (It does not, of course, contradict the variation principle!)

But the difference between (28) and the empirically better substantiated result (27) is to be accounted for by the inclusion of the dipole-quadrupole interaction. A method for estimating the latter has been given.[18] It involves the use of a *one*-term dispersion formula. To adapt it to

TABLE V. Quadrupole moment of H_2 (in units ea_0^2) as a function of Z.

Z	1	1.166	1.428	1.785
$-Q'$	0.284	0.252	0.200	0.137

TABLE VI. Quadrupole energy (E_Q) as function of intermolecular separation (R).

S	R (in A)	E_Q (in volts) Pos. a	Pos. b	Pos. c
$Z=1.428$				
6	2.22	0.000962	−.000481	0.000361
7	2.59	0.000445	−.000223	0.000167
8	2.96	0.000228	−.000114	0.0000857
9	3.33	0.000127	−.0000634	0.0000475
10	3.70	0.0000748	−.0000374	0.0000281
11	4.07	0.0000465	−.0000232	0.0000174
$Z=1.785$				
6	1.78	0.00134	−.000672	0.000504
7	2.07	0.000632	−.000316	0.000236
8	2.37	0.000321	−.000160	0.000120
9	2.66	0.000180	−.0000901	0.0000676
10	2.96	0.000106	−.0000528	0.0000396
11	3.25	0.0000662	−.0000331	0.0000248

[16] This, in a sense, counteracts the simplification made in the exchange integrals leading to Eq. (22).

[17] K. L. Wolf and K. F. Herzfeld, *Handbuch der Physik* (1928), Vol. 20.

[18] H. Margenau, J. Chem. Phys. **6**, 896 (1938).

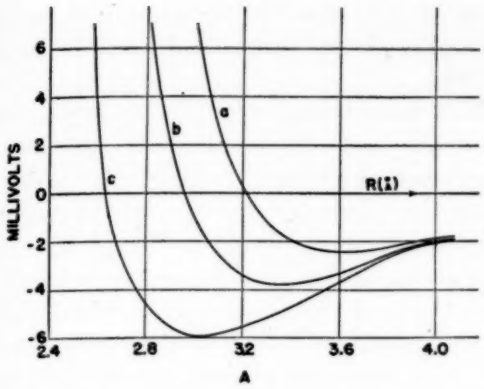

FIG. 2. Interaction energies when the approximately "right" value of Z ($Z=1.428$) is used.

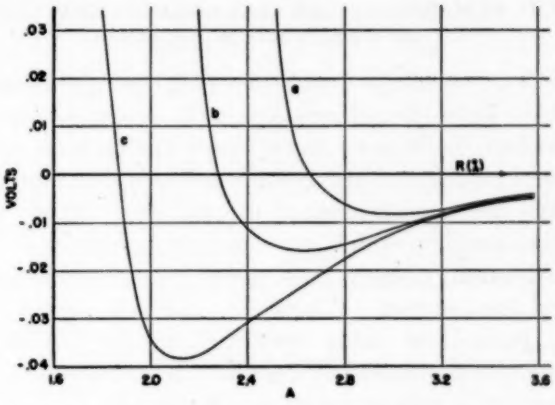

FIG. 3. Curves similar to those in Fig. 2 but with the "wrong" value of Z ($Z=1.785$).

the problem at hand, we shall take mean values of the f's and ΔE's in Herzfeld and Wolf's expression obtaining the contribution

$$-31\times10^{-76}/R^8 \text{ erg.}$$

When this is added to (28), and both terms are expressed in ev, we have

$$\bar{E}_{\text{v.d.w}}=-\left(\frac{6.38}{R^6}+\frac{19.4}{R^8}\right)\text{ volts,} \qquad (29)$$

provided R is measured in A. At $R=3$A, the d.-q. term contributes about $\frac{1}{3}$, at $R=2.5$A about $\frac{1}{2}$ as much as the d.-d. term. If, therefore, we wished to approximate (29) by means of a single term proportional to R^{-6} as is often done, we should in this range of R (where the van der Waals minimum occurs) increase the d.-d. contribution by about 40 percent, thus obtaining

$$\bar{E}_{\text{v.d.w}}=-\frac{9.0}{R^6}\text{ volts}=-\frac{15.4}{R^6}\frac{e^2}{a_0}\left(\frac{a_0}{R}\right)^6. \qquad (29a)$$

This is not far from the result (27) which was obtained by Massey and Buckingham for the d.-d. interaction alone.

VII. SUMMARY OF RESULTS

In Figs. 2 and 3 we have compounded the partial interaction energies represented by Eqs. (22), (26), and (29) or (29a), obtaining a graph which expresses the total repulsive-attractive behavior of the molecules. Figure 2, drawn for what we have determined to be the approximately "right" value of Z, should be about correct. Figure 3, on the other hand, based on the "wrong" value of Z, is presented to show the effect of this choice. In view of the uncertainty in this parameter, it is difficult to estimate the accuracy of our exchange force calculation, but we believe it to be not greatly inferior to the accuracy with which the long range van der Waals forces can be obtained.

The shape of the molecule is reflected in the relative positions of the three minima, the one implying end-on collisions being much farther out than that for broadside collisions. Interesting also is the fact that the minima are of entirely different depths. In actual impact problems, an average of the three behaviors here depicted will have to be considered.

Comparison with experimental facts can at present only be made in an indirect way. Lennard-Jones and his collaborators[19] have analyzed available measurements of the second virial coefficient of H_2. The procedure is based on the assumption that the interaction energy can be represented sufficiently well by a *single* function of spherical symmetry and of the form $(\nu/R^n)-(\mu/R^6)$. It is found that the data can be accommodated by several values of the exponent n. The curves obtained have minima in the region from 3.3 to 3.5A, and depths at minimum ranging from 2.7 to 2 millivolts. If curve b of Fig. 2 is taken to be illustrative of the "mean" behavior, the agreement with the results of Lennard-Jones is rather satisfactory.

[19] See R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, 1939).

VIII. REMARKS ON THE EXCHANGE INTERACTION OF TWO HELIUM ATOMS

The exchange forces between helium atoms have been the subject of several investigations;[1] in fact the Wang function used in this work has been applied to the helium problem by Gentile. We are here interested in only one feature of this problem which appears to have received no attention, namely the dependence of the forces on the assumed value of Z.

Instead of using published results[20] (which seem to be somewhat disfigured by typographical errors) it will be found simpler for our purposes to start anew and use our compact notation. The ground state of a single helium atom is represented by

$$\psi_0 = |a\alpha \quad a\beta|.$$

This leads, by simple steps, to the energy

$$E_0 = H_{00} = 2D - 2(2-Z)A + (aa\rho aa). \quad (30)$$

If now we note that

$$D = -\tfrac{1}{2}Z^2, \quad A = Z, \quad (aa\rho aa) = \tfrac{5}{8}Z, \quad (31)$$

all in units e^2/a_0, then (30) will become a minimum for $Z = 27/16$, a fact which is well known.

In the interaction problem, the ground state of the two atoms is described by

$$\psi = |a\alpha \quad a\beta \quad c\alpha \quad c\beta|.$$

Here the total energy becomes

$$E = \bar{H}/\epsilon$$

with

$$\bar{H} = (aacc|H|aacc) - 2(caac|H|aacc) + (ccaa|H|aacc)$$

$$\epsilon = (1-\Delta^2)^2,$$

$$\Delta = \int acd\tau.$$

Thus we find

$$\begin{aligned}(1-\Delta^2)^2 E = {} & 2(1-\Delta^2)^2 E_0 + 4C \\ & - 2\Delta^2[B + C + X + 2(2-Z)A - 2(aa\rho aa) \\ & - 2(3-Z)T + 4(aa\rho ac)/\Delta] \\ & + \Delta^4[4(2-Z)A - 2(aa\rho aa) + 4X \\ & - 4(2-Z)T + 2(ac\rho ca)/\Delta^2] \quad (32)\end{aligned}$$

where all functions without subscripts now refer to the interatomic distance R, and E_0 is given by (30).

With the neglect of terms in Δ^4, this expression could also have been obtained—though with more labor—by letting the distance s in Eq. (21) go to zero. Now it is permissible to neglect Δ^4 and hence the last row of (32). Since the function C is always much smaller and decreases faster than Δ^2, the contribution to the exchange energy comes almost entirely from the second row of (32). The only terms inside the bracket multiplying Δ^2 which do not vanish as R becomes large are

$$2(2-Z)A - 2(aa\rho aa).$$

If, therefore, we wish $E - 2E_0$ to be positive, we must require

$$(aa\rho aa) > (2-Z)A.$$

In view of Eqs. (31) this implies $Z > 11/8$. The mathematical situation encountered in the H_2 problem when Z was chosen to be 1.166 is thus explained. Whether this phenomenon has any physical interest, as for example in the interaction between two negative ions of atomic hydrogen where Z is certainly smaller than the limiting value, is perhaps difficult to say.

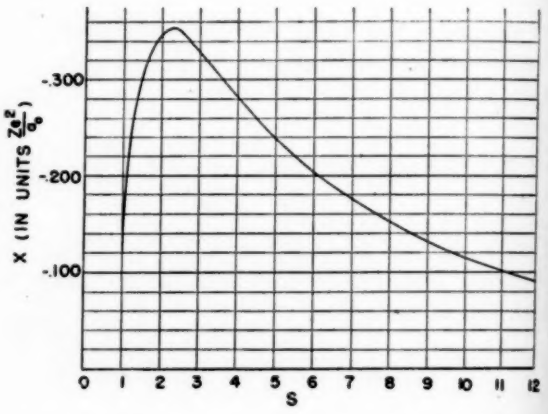

FIG. 4. Graph for the determination of X in terms of S.

The author wishes to acknowledge gratefully the computational help given him by two undergraduate students, C. E. Hummel and R. A. Peck.

[20] G. Gentile, Zeits. f. Physik **63**, 795 (1930).

APPENDIX

A list of the more important functions encountered in this paper is here appended.

$$S=ZR/a_0,$$

$$\Delta=e^{-S}(1+S+S^2/3),$$

$$B=(Ze^2/a_0)(1+S^{-1})e^{-2S},$$

$$C=\frac{Ze^2}{a_0}\left(S^{-1}+\frac{5}{8}-\frac{3}{4}S-\frac{S^2}{6}\right)e^{-2S},$$

$$T=\frac{Ze^2}{a_0}(1+S)\Big/\left(1+S+\frac{S^2}{3}\right).$$

X is a more complicated function involving Sugiura's integral. In terms of the functions used and defined in Pauling and Wilson,[21]

$$X=\frac{Ze^2}{a_0}\left(\frac{1}{S}+\frac{2K(S)}{\Delta(S)}+\frac{K'(S)}{\Delta^2(S)}\right).$$

For calculations, the graph of X given in Fig. 4 will be found more convenient.

[21] L. Pauling and E. B. Wilson, fr., *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, New York). See p. 342 et seq.

PHYSICAL REVIEW VOLUME 64, NUMBERS 5 AND 6 SEPTEMBER 1 AND 15, 1943

The Energies of the γ-Rays from Radioactive Scandium, Gallium, Tungsten, and Lanthanum

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(Received June 10, 1943)

The energies of some γ-rays have been determined by the method of semicircular focusing of Compton recoils in a magnetic spectrograph. The results thus obtained are as follows:

Radioelement	Sc^{48}	Ga^{72}	W^{187}	La^{140}
Quantum energies (Mev)	1.35±0.03	1.17±0.02, 2.65±0.06	0.94±0.02	2.04±0.04

The two quanta emitted in the disintegration of Ga^{72} are present with equal intensity, which suggests that they may be in cascade. The γ-ray activity of Ga^{72} was followed for 100 hours and was found to decay with a half-period of 14.25±0.20 hr.

INTRODUCTION

THE energies of the γ-rays emitted in the disintegration of several radio-elements have been measured by means of a magnetic spectrograph which has been previously described.[1] Compton recoil electrons are focused by a magnetic field, and coincidences are then observed as a function of $H\rho$. The radius of curvature of the path of the recoils is 5.50 cm.

Because of the fact that slow electrons are heavily absorbed and scattered from the focused beam by the walls of the counters and by the argon-alcohol counter mixture which is present throughout the magnet box, it has been found advisable to employ double coincidence counting, using the counters T_1 and T_2 (Fig. 1, reference 1), when making observations on quanta of an energy less than 1 Mev. Triple coincidence counting, with the counters T_1, T_2, and T_3, is especially suitable for obtaining end points of distributions in regions of higher energy (greater than 1 Mev), since the gamma-ray background is then very small. The absorption of the slow electrons also leads to a lower limit of satisfactory measurement. The recoils arising from γ-rays of energy less than about 0.5 Mev are not observable.

The treatment of the background count and the corrections which are applied to data obtained with this spectrograph have been previously outlined[1] and are obviously the same,

*At present at the Radiation Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts.

[1] C. E. Mandeville, Phys. Rev. **62**, 309 (1942); Phys. Rev. **63**, 387 (1943).

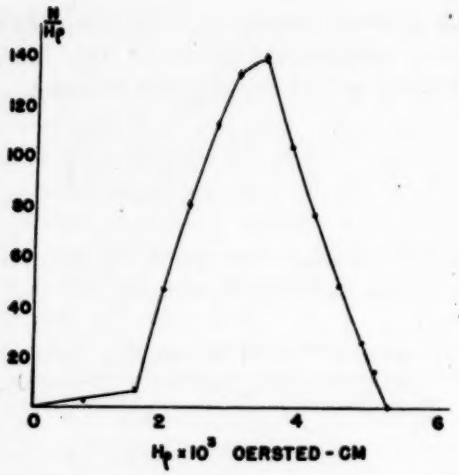

FIG. 1. Momentum distribution of the Compton recoils of the γ-rays from Sc^{48}. The Sc^{48} of this curve was produced by a bombardment of CaF_2 by deuterons of energy 12 Mev. Triple coincidences in the counters T_1, T_2, and T_3 were recorded.

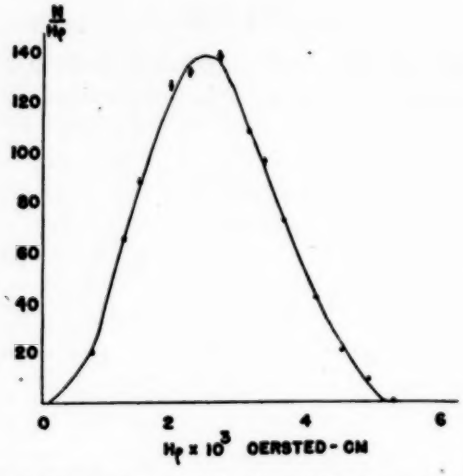

FIG. 2. Momentum distribution of the Compton recoils of the γ-rays from Sc^{48}. The Sc^{48} of this curve was produced by the reaction $Ti^{48}(n,p)Sc^{48}$. Double coincidences in the counters T_1 and T_2 were recorded.

whether double or triple coincidences are recorded.

In all instances under discussion in this paper, observations were begun at a time not less than twenty-four hours after cessation of bombardment.

Sc^{48}

The γ-rays from Sc^{48} have been discussed in a preliminary report.[2] The momentum distribution of the Compton recoils of the γ-rays from Sc^{48} produced by a bombardment of calcium fluoride by deuterons of energy 12 Mev is given in Fig. 1. The energy of the γ-ray taken from the end point of the distribution is found to be 1.35 ± 0.03 Mev. The ordinates of the distribution were found to decay with the established 44-hr. half-period[3] of Sc^{48}. In obtaining the curve of Fig. 1, triple coincidences were recorded. The electrons of low energy are seen to be heavily absorbed on the interval $0<H\rho<2000$.

Pure titanium dioxide was bombarded by fast neutrons from the reaction *Be–d–n*. The momentum distribution of the Compton recoils of the γ-rays from Sc^{48} formed by the reaction $Ti^{48}(n,p)Sc^{48}$ is given in Fig. 2. The quantum energy obtained from the end point of the distribution is again found to be 1.35 ± 0.03 Mev. Double coincidences were recorded.

Hibdon, Pool, and Kurbatov[4] have likewise found Sc^{48} to be a gamma-ray emitter, and their absorption experiments indicate a quantum energy of 1.33 Mev.

Ga^{72}

Pure metallic gallium has been irradiated by slow neutrons. The γ-ray activity was followed

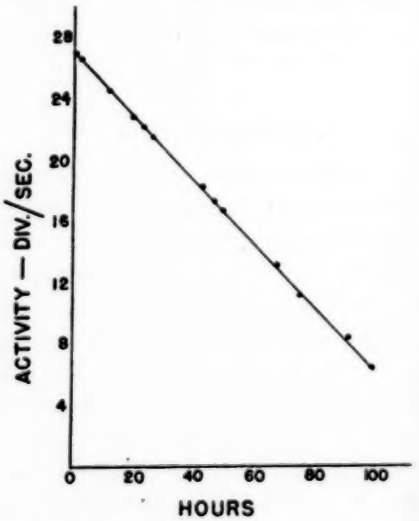

FIG. 3. Decay of gamma-ray activity of Ga^{72}. The half-period taken from the slope of the curve is 14.25 ± 0.20 hr.

[2] C. E. Mandeville, Phys. Rev. **62**, 555 (1942).
[3] H. Walke, Phys. Rev. **57**, 163 (1940).
[4] C. T. Hibdon, M. L. Pool, and J. D. Kurbatov, Phys. Rev. **63**, 462 (1943).

for one hundred hours with a Lauritsen electroscope, and the half-period taken from the slope of the decay curve of Fig. 3 was found to be 14.25±0.20 hours, in good agreement with the value 14.1±0.2 hr. obtained by Sagane.[5] The momentum distribution of the Compton recoils of the γ-rays from Ga^{72} is given in Fig. 4, where it is seen that two quanta of energies 1.17±0.02 Mev and 2.65±0.06 Mev are emitted with equal intensity, suggesting that they may be in cascade.

It is of interest to note that Sagane *et al.*,[6] using cloud chamber and magnetic field, have found the K–U extrapolated limit of the β-rays from the negatron emitting Ga^{72} to be 1.71 Mev, whereas absorption experiments by Livingood and Seaborg[7] have indicated a maximum β-ray energy of 2.6 Mev. The disagreement between the two results might be related to secondary effects arising from the 2.65 Mev γ-ray from Ga^{72}. The influence of Compton recoils from γ-rays of high energy upon absorption measurements of the energies of primary β-rays has been discussed in several recent publications.[8-10]

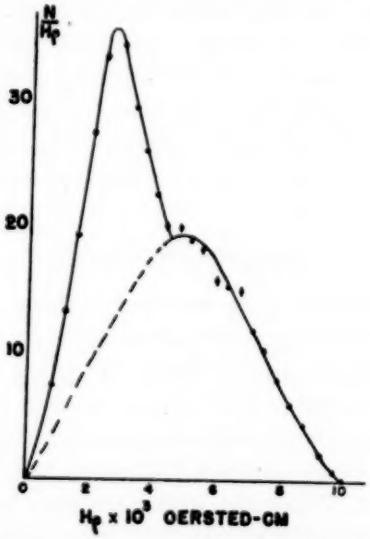

FIG. 4. Momentum distribution of the Compton recoils of the γ-rays from Ga^{72}. The two electron groups correspond to two equally intense quanta having energies of 1.17±0.02 Mev and 2.65±0.06 Mev.

[5] R. Sagane, Phys. Rev. **55**, 31 (1939).
[6] R. Sagane, S. Kojima, and G. Miyamoto, Proc. Phys. Math. Soc. Japan **21**, 728 (1939).
[7] J. J. Livingood and G. T. Seaborg, Rev. Mod. Phys. **12**, 30 (1940).
[8] M. Deutsch, Phys. Rev. **61**, 672 (1941).
[9] M. Deutsch, J. R. Downing, L. G. Elliot, J. W. Irvine, Jr., and A. Roberts, Phys. Rev. **62**, 3 (1942).
[10] Lise Meitner, Phys. Rev. **63**, 73 (1943).

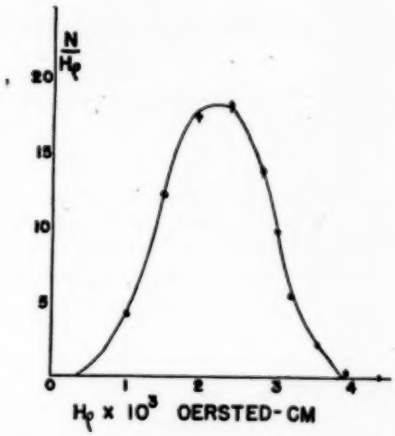

FIG. 5. Momentum distribution of the Compton recoils of the γ-rays from W^{187}.

W^{187}

The radioactive tungsten isotope of half-period 24.1 hours[11] was produced when pure powdered tungsten was irradiated by slow neutrons. The momentum distribution of the Compton recoils of the γ-rays from W^{187} is given in Fig. 5. The quantum energy as determined from the end point of the distribution was found to be 0.94 ±0.02 Mev. The energy of this γ-ray has been previously reported to be 0.87±0.03 Mev by lead absorption,[11] and aluminum absorption of the Compton recoils of this γ-ray has led to a quantum energy of 0.90 Mev.[12] From the shape of the curve of Fig. 5, it is clear that the γ-ray of energy 0.94 Mev is the only γ-ray present with an energy greater than 0.5 Mev.

Evidence for the emission by W^{187} of γ-rays of an energy less than 0.5 Mev has also been obtained.[12, 13]

La^{140}

The γ-rays emitted by the 40-hr.[14] La^{140} have been discussed in a previous report.[1] The γ-ray activity of pure La_2O_3 irradiated by slow neutrons was followed for 160 hours and was found to decay with a half-period of 40.8±1.0 hr. The decay curve is given in Fig. 6. The momentum

[11] Kasimir Fajans and W. H. Sullivan, Phys. Rev. **58**, 276 (1940).
[12] Arnold F. Clark, Phys. Rev. **61**, 242 (1942).
[13] G. E. Valley, Phys. Rev. **59**, 686 (1941).
[14] K. E. Weimer, M. L. Pool, and J. D. Kurbatov, Phys. Rev. **63**, 67 (1943).

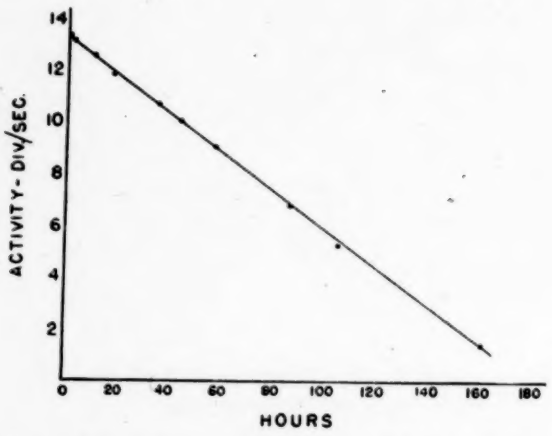

FIG. 6. Decay of gamma-ray activity of La_2O_3 irradiated by slow neutrons. The half-period taken from the slope of the curve is 40.8 ± 1.0 hr.

distribution of the Compton recoils of the γ-rays from La^{140} is to be seen in Fig. 7, and the quantum energy of the single γ-ray present was found to be 2.04 ± 0.04 Mev, in good agreement with the previously determined absorption value of 2.00 ± 0.05 Mev.[14]

It is not as yet certain whether La^{140} may be regarded as a source of absolutely monochromatic 2.04-Mev radiation, since recent coincidence experiments[15] by W. C. Peacock of The Massachusetts Institute of Technology seem to indicate that a γ-ray of energy less than 0.3 Mev is in cascade with the 2.04-Mev quantum. These coincidence experiments were only of a preliminary nature, however, and are not yet to be regarded as conclusive.

OTHER REMARKS

Sc^{48} and La^{140} appear to be, for the most part, emitters of monochromatic gamma-radiation. It is suggested, therefore, that the γ-rays of these elements might be used for the determination of the exact shape of the momentum distribution of the Compton recoils of a single γ-ray at the outset of experiments in which spectrographs of this type or related types are employed. A knowledge of the shape of the distribution arising from a single γ-ray is particularly desirable, since a misunderstanding of the nature of the distribution may lead to an erroneous interpretation of results obtained from an examination of emitters of complex gamma-ray spectra.[1]

[15] M. Deutsch, private communication.

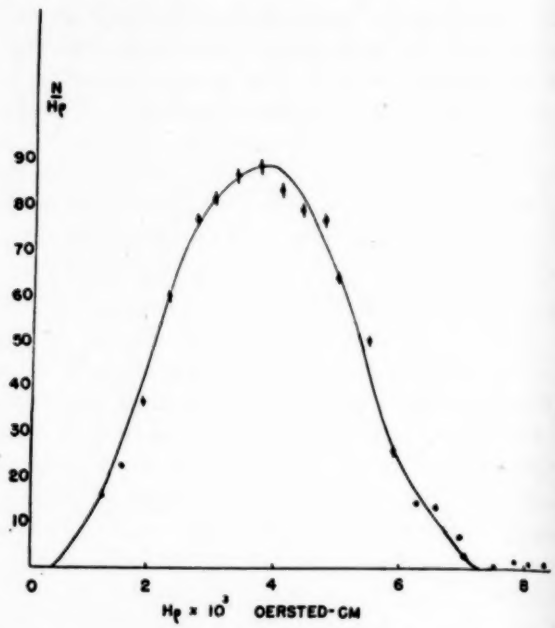

FIG. 7. Momentum distribution of the Compton recoils of the γ-rays from La^{140}.

ACKNOWLEDGMENTS

The writer wishes to point with emphasis to the fact that the radioactive isotopes discussed in this paper were without exception prepared by the members of the cyclotron group of Washington University, St. Louis, Missouri. The splendid cooperation of Professor A. L. Hughes, Mr. H. W. Fulbright, and other members of the Washington University cyclotron group made possible these investigations.

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The Spectra of the Rare Gases and their Zeeman Effects

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The Zeeman effect of the rare gases is discussed from the standpoint of the coupling scheme of Shortley and Fried. The matrices for this type of interaction are calculated and also the g factors from the transformations to LS coupling for the p^5f configurations. These enable us to determine the Paschen-Back patterns to be expected. The calculated patterns are compared with observed structures and the agreement is very satisfactory in most cases.

WE have become so accustomed to hearing the phrase "transition from LS to jj coupling" that whenever we think of the variation in coupling in a series of levels, we automatically think of the change taking place from the LS condition toward a jj coupling limit. The spectra of the rare gases afford examples which show that this simple picture is inadequate. The work of Shortley and Fried[1] has shown that in the spectra of Cu II and A, a very striking example of a special type of intermediate coupling exists. This may be shown by calculations which neglect all parameters in the energy matrix excepting F_2 and ζ_p. This is equivalent to assigning a J value to the core (p^5) and using only one electrostatic parameter in addition. The result is to break up the spectrum into two widely separated groups ($^2P_{3/2}$ and $^2P_{1/2}$ of the p^5 core) each of these in turn being broken up into a group of closely-packed levels. These closely-packed levels in turn exhibit the peculiarity of being levels with multiple J values. Shortley and Fried[1] applied their results only to the spectrum of argon among the rare gases, but since then a considerable amount of data on the Zeeman effect has been published which helps to substantiate this picture.

Some years ago,[2] the author had occasion to investigate the genealogy of the p^5p configurations of the rare gases as it could be determined from the g factors. Satisfactory curves could be drawn for the values known up to that time showing the transition from LS coupling toward jj coupling, but the slopes of some of the curves seemed to be too abrupt at the jj end. Since that time, a large amount of data on the p^5d and some data on the p^5f configurations have been given.[3] It was primarily the data on the p^5f configuration which led to the considerations discussed in this paper.

Table I gives the matrices for the transformation from LS to jj coupling of the p^5f configuration, together with the g values to be derived from it by performing the operation

$$g(\alpha J)=\sum_{\gamma SL} g(SLJ)(\gamma SLJ|\alpha J)^2. \qquad (1)$$

Thus, to find the g value corresponding to a particular row JJ', square the numbers appearing in that row and multiply each of the numbers thus obtained by the $g(SLJ)$ occurring below the LS designation at the head of the column in which the number lies. Add all the terms thus obtained and this will be the g value for jj coupling. This same method applied to the transformation matrix between any other type of coupling and LS coupling will yield the g value for that type of coupling.

It is, of course, not necessary to perform these laborious calculations for the sole purpose of determining the g factors in any limiting case of coupling. Closed formulas for the calculation of g factors have been given for a number of these.[4] But for the calculations of intensities and energy levels in intermediate fields, the complete matrix must be known.[5]

[1] G. H. Shortley and B. Fried, Phys. Rev. **54**, 749 (1938).
[2] J. B. Green, Phys. Rev. **52**, 736 (1937).

[3] Summary bibliographies may be found as follows: (a) Neon: J. B. Green and J. A. Peoples, Phys. Rev. **54**, 602 (1938). (b) Argon: J. B. Green and B. Fried, Phys. Rev. **54**, 876 (1938). (c) Krypton: Green, Bowman, and Hurlburt, Phys. Rev. **58**, 1094 (1940). (d) Xenon: Green, Hurlburt, and Bowman, Phys. Rev. **59**, 72 (1941).
[4] See, e.g., Pauling and Goudsmit, *The Structure of Line Spectra* (McGraw-Hill, New York, 1930).
[5] G. Racah, Phys. Rev. **61**, 537 (1942) has used the vector coupling method to calculate g formulas for this

TABLE I. Matrices for transformation from LS to jj coupling for p^5f.

			$^3G_5$	$g(jj)$	
a	$\frac{3}{2}$	$\frac{7}{2}$	1	1.200	$J=5$
$g(LS)$			1.200		

			$^3G_4$	$^3F_4$	$^1G_4$		$g(jj)$	
a	$\frac{3}{2}$	$\frac{7}{2}$	2	$2(15)^{\frac{1}{2}}$	$2\sqrt{5}$		1.181	
b	$\frac{3}{2}$	$\frac{5}{2}$	$3\sqrt{5}$	$\sqrt{3}$	-6	$\cdot\frac{1}{2\sqrt{21}}$	1.034	$J=4$
c	$\frac{1}{2}$	$\frac{7}{2}$	$(35)^{\frac{1}{2}}$	$-(21)^{\frac{1}{2}}$	$2\sqrt{7}$		1.083	
$g(LS)$			1.050	1.250	1.000			

			$^3G_3$	$^3F_3$	$^3D_3$	$^1F_3$		$g(jj)$	
a	$\frac{3}{2}$	$\frac{7}{2}$	-6	$6\sqrt{7}$	$-12\sqrt{5}$	$6(21)^{\frac{1}{2}}$		1.142	
b	$\frac{3}{2}$	$\frac{5}{2}$	$9\sqrt{5}$	$5(35)^{\frac{1}{2}}$	-8	$-2(105)^{\frac{1}{2}}$		0.997	
c	$\frac{1}{2}$	$\frac{7}{2}$	$-3\sqrt{3}$	$5(21)^{\frac{1}{2}}$	$8(15)^{\frac{1}{2}}$	$6\sqrt{7}$	$\cdot\frac{1}{42}$	1.202	$J=3$
d	$\frac{1}{2}$	$\frac{5}{2}$	36	$-4\sqrt{7}$	$2\sqrt{5}$	$4(21)^{\frac{1}{2}}$		0.825	
$g(LS)$			.750	1.083	1.333	1.000			

			$^3F_2$	$^3D_2$	$^1D_2$		$g(jj)$	
a	$\frac{3}{2}$	$\frac{7}{2}$	$-\sqrt{3}$	$2\sqrt{6}$	6		1.047	
b	$\frac{3}{2}$	$\frac{5}{2}$	$4\sqrt{2}$	5	$-\sqrt{6}$	$\cdot\frac{1}{3\sqrt{7}}$	0.897	$J=2$
d	$\frac{1}{2}$	$\frac{5}{2}$	$2\sqrt{7}$	$-(14)^{\frac{1}{2}}$	$(21)^{\frac{1}{2}}$		0.889	
$g(LS)$			0.667	1.167	1.000			

			$^3D_1$	$g(jj)$	
b	$\frac{3}{2}$	$\frac{5}{2}$	1	0.500	$J=1$
$g(LS)$			0.500		

Table II gives the matrices of the electrostatic parameter F_2, the only one to be considered in

type of coupling, but they give the same result as the $\{[(l_1s_1)l_2]s_2\}$ formulas that are given in Pauling and Goudsmit (reference 4), or Candler, *Atomic Spectra* (Cambridge Univ. Press, 1937, p. 143–145).

TABLE II. Matrices of electrostatic energy F_2 in jj coupling for p^5f.

$-F_0+$

	$5a$		
$5a$	$-5F_2$		$J=5$

	$4a$	$4b$	$4c$	
$4a$	$\frac{65}{7}F_2$	$\frac{\sqrt{5\cdot 10}}{7}F_2$	$-\frac{10(35)^{\frac{1}{2}}}{7}F_2$	
$4b$		$-\frac{30}{7}F_2$	$-\frac{5\sqrt{7}}{7}F_2$	$J=4$
$4c$			0	

	$3a$	$3b$	$3c$	$3d$	
$3a$	$\frac{25}{7}F_2$	$-\frac{6\sqrt{5}}{7}F_2$	$\frac{50\sqrt{3}}{7}F_2$	$\frac{30}{7}F_2$	
$3b$		$\frac{66}{7}F_2$	$\frac{9(15)^{\frac{1}{2}}}{7}F_2$	$-\frac{24\sqrt{5}}{7}F_2$	$J=3$
$3c$			0	0	
$3d$				0	

	$2a$	$2b$	$2d$	
$2a$	$-\frac{75}{7}F_2$	$-\frac{12\sqrt{6}}{7}F_2$	$-\frac{6(21)^{\frac{1}{2}}}{7}F_2$	
$2b$		$\frac{12}{7}F_2$	$\frac{24(14)^{\frac{1}{2}}}{7}F_2$	$J=2$
$2d$			0	

	$1b$	
$1b$	$-12F_2$	$J=1$

TABLE III. Transformation matrices from jj to intermediate coupling.

	$4a$	$4b$	
$4a'$	$(20)^{\frac{1}{2}}$	1	$\cdot\frac{1}{(21)^{\frac{1}{2}}}$
$4b'$	-1	$(20)^{\frac{1}{2}}$	

	$3a$	$3b$	
$3a'$	2	$-3\sqrt{5}$	$\cdot\frac{1}{7}$
$3b'$	$3\sqrt{5}$	2	

	$3c$	$3d$	
$3c'$	$4\sqrt{3}$	1	$\cdot\frac{1}{7}$
$3d'$	-1	$4\sqrt{3}$	

	$2a$	$2b$	
$2a'$	$\sqrt{3}$	$-4\sqrt{2}$	$\cdot\frac{1}{35}$
$2b'$	$4\sqrt{2}$	$\sqrt{3}$	

this example, and if the determinants of these matrices are solved, they yield the following results, after adding the electromagnetic parameter ζ_p to the higher set (c and d), and subtracting $\frac{1}{2}\zeta_p$ from the lower set (a and b).

$$\begin{aligned}
&\text{Upper set } 4c,\ 3c,\ 3d,\ 2d = -F_0+\zeta_p.\\
&\text{Lower set } 5a,\ 4b' = -F_0-\tfrac{1}{2}\zeta_p- 5F_2,\\
&\qquad 4a',\ 3a' = -F_0-\tfrac{1}{2}\zeta_p+10F_2,\\
&\qquad 3b',\ 2a' = -F_0-\tfrac{1}{2}\zeta_p+ 3F_2,\\
&\qquad 2b',\ 1b = -F_0-\tfrac{1}{2}\zeta_p-12F_2.
\end{aligned} \tag{1}$$

These solutions, inserted in Table II, give the transformation matrices for jj coupling to this particular variety of intermediate coupling and are given in Table III. When we apply these transformations to the matrices of Table I we arrive at Table IV, which gives the transformation from LS to this intermediate type of coupling. Listed with Table IV are the g values for this special coupling scheme. A striking difference is shown between the g values for the intermediate case and those for jj coupling, even though they seem to be quite close together at first glance. Perhaps even more striking is the difference of phase between several homologous elements of the two sets of matrices.

A study of the p^5f configurations of the rare gases from the standpoint of Eqs. (1) shows some interesting points.[6]

Neon

Strangely enough the spectrum of neon shows the least conformity with the above results. The levels labeled W (except $4W$) are separated from the others of the lower ($^2P_{3/2}$) set by about 100 cm^{-1}. Except for $4W$, all the members of the upper set are piled together, as indicated by (1). The author is of the opinion that interaction with the p^5p configurations is not sufficiently large to account for such large perturbations, and suggests that some revision of these assignments is necessary.

Argon

As indicated by Shortley and Fried[1] the p^5f configurations of argon represent an almost perfect example of the application of Eqs. (1). Each of the levels of the lower ($^2P_{3/2}$) set can be assigned a double J value, and the spacings of the four observed levels are in almost perfect accord with the theory. The upper ($^2P_{1/2}$) set should consist of four levels lumped into one, but evidence of splitting into two levels is noticed.

Krypton

In krypton, we see for the first time the splitting of the levels of the lower ($^2P_{3/2}$) set into pairs. This appears as a separation of the lowest level ($J=1, 2$) into two separate levels (X, Z); and of the third ($J=2, 3$) into two separate (but

TABLE IV. Matrices for transformation from LS to intermediate coupling.

	$^3G_5$	$g(jj)$	
$5a'$	1	1.200	$J=5$
$g(LS)$	1.200		

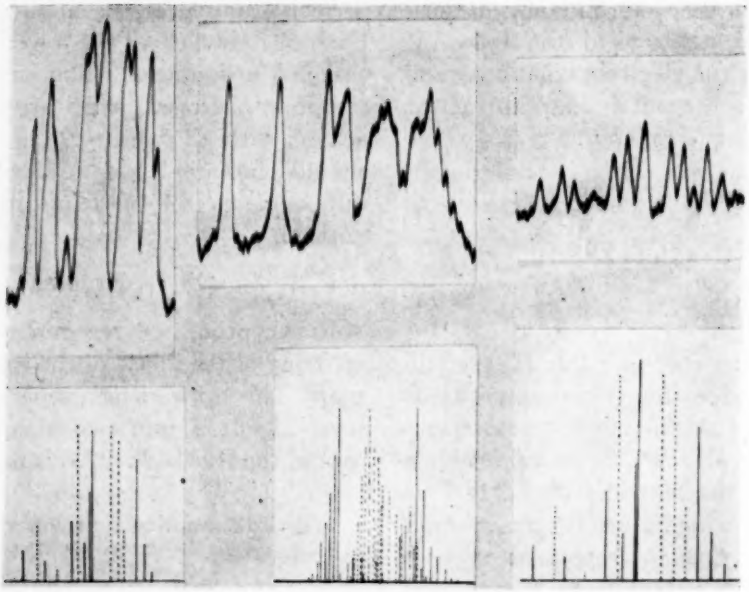
	$^3G_4$	$^3F_4$	$^1G_4$		g(Int.)	
$4a'$	$\sqrt{5}$	$3\sqrt{3}$	2		1.195	
$4b'$	4	0	$-2\sqrt{5}$	$\cdot\frac{1}{6}$	1.022	$J=4$
$4c'$	$(15)^{\frac{1}{2}}$	-3	$2\sqrt{3}$		1.083	
$g(LS)$	1.050	1.250	1.000			

	$^3G_3$	$^3F_3$	$^3D_3$	$^1F_3$		g(Int.)	
$3a'$	-21	$-9\sqrt{7}$	0	$6\sqrt{21}$		0.964	
$3b'$	0	$4(35)^{\frac{1}{2}}$	-28	$2(105)^{\frac{1}{2}}$	$\cdot\frac{1}{42}$	1.175	$J=3$
$3c'$	0	$8\sqrt{7}$	$14\sqrt{5}$	$4(21)^{\frac{1}{2}}$		1.206	
$3d'$	$21\sqrt{3}$	$-3(21)^{\frac{1}{2}}$	0	$6\sqrt{7}$		0.821	
$g(LS)$	.750	1.083	1.333	1.000			

	$^3F_2$	$^3D_2$	$^1D_2$		g(Int.)	
$2a'$	-5	$-2\sqrt{2}$	$2\sqrt{3}$		0.844	
$2b'$	0	$3\sqrt{3}$	$3\sqrt{2}$	$\cdot\frac{1}{3\sqrt{5}}$	1.100	$J=2$
$2d'$	$2\sqrt{5}$	$-(10)^{\frac{1}{2}}$	$(15)^{\frac{1}{2}}$		0.889	
$g(LS)$	.667	1.167	1.000			

	$^3D_1$	g(Int.)	
$1b'$	1	0.500	$J=1$
$g(LS)$	.500		

[6] W. F. Meggers and C. J. Humphreys, Bur. Stand. J. Research **10**, 427 (1933) (RP 540). C. J. Humphreys and W. F. Meggers, Bur. Stand. J. Research **10**, 139 (1933) (RP 521). C. J. Humphreys, J. Research Nat. Bur. Stand. **20**, 17 (1938) (RP 1061).



(a) (b) (c)

FIG. 1. (a) λλ 6178–9, Xe $1s_2-5Y$, $5X$. (b) λλ 7584, Xe $3d_4'-5T$, $5Z$. (The lines to the right of the figure are Kr.) (c) λλ 7472–4, Xe $3d_5-5Y$, $5X$. Above are shown microphotograms of original plates; below are shown calculated patterns. Full lines are perpendicular polarizations; dotted lines parallel polarizations; dot and dash, mixed polarizations.

very close) levels (Y, T). $5X$ and $5Z$ are perturbed by the upper terms of $p^5 3p$ and are therefore more widely separated than we should expect. No levels of the upper ($^2P_{1/2}$) set are known for krypton.

Xenon

This is probably the best known spectrum as far as the $p^5 f$ configurations are concerned. The members of the lower set are all separated with the exception of the highest (W), but lines involving these levels show Paschen-Back effect, indicating that the W levels are complex. All of the levels of the upper ($^2P_{1/2}$) set lie in the negative energy region and none has been found.

Lines involving the $p^5 f$ configurations in neon and argon did not appear on the plates. A few of these lines appeared on the krypton plates, and many of them on the xenon plates.

Examples of the Paschen-Back effect of xenon chosen for this paper were the $p^5 5f(2b', 1b)$ and the $p^5 5f(5a, 4b')$ known as $5Y$, $5X$ and $5T$, $5Z$, respectively. These particular levels were chosen because each pair contains one pure level ($5X = {}^3D_1$ and $5T = {}^3F_5$). The results are shown in the accompanying figure. The method of making these calculations has been outlined in a

TABLE V. g values for $p^5 p$ of rare gases.

$J=1$	p_{10}	Ne	1.984	1.929			Limits
		A	1.985	1.90			JJ 1.500
		Kr	1.898	1.834	1.795	1.795	Int. 1.778
		Xe	1.852	1.728*	1.801		
$J=1$	p_7	Ne	0.669	0.974			
		A	0.838	1.01			JJ 1.333
		Kr	1.004	1.034	1.041	1.014	Int. 1.056
		Xe	1.022	0.903*	1.036		
$J=1$	p_5	Ne	0.999	0.685			
	p_4	A	0.819	0.61			JJ 0.667
	p_4	Kr	0.647	0.648			Int. 0.611
	p_4	Xe	0.790*				
$J=1$	p_2	Ne	1.340	1.397			
	p_2	A	1.380	1.45			JJ 1.500
	p_2	Kr	1.452	1.401			Int. 1.556
	p_2	Xe	1.552*				
$J=2$	p_4	Ne	1.301	1.184			
	p_3	A	1.260	1.18			JJ 1.067
	p_3	Kr	1.181	1.158			Int. 1.067
	p_3	Xe	1.195				
$J=2$	p_6	Ne	1.229	1.360			
	p_6	A	1.305	1.42			JJ 1.333
	p_6	Kr	1.388	1.403	1.403	1.411	Int. 1.433
	p_6	Xe	1.379	1.347	1.395	1.386	
$J=2$	p_8	Ne	1.137	1.112			
	p_8	A	1.112	1.09			JJ 1.167
	p_8	Kr	1.099	1.107			Int. 1.067
	p_9	Xe	1.106	1.123	1.103		

* These levels from different configurations are close enough to perturb each other.

TABLE VI. g values for p^5d configurations of the rare gases.

								Limits	
$J=1$	s_1'	Ne	0.752	0.797				JJ	0.833
		A	0.877	0.768				Int.	0.833
$J=1$	d_2	Ne	0.860	0.812	0.791				
		A	0.768	0.813	(1.186)?			JJ	1.110
		Kr	0.935	0.823	0.797			Int.	0.833
		Xe	0.919	0.914	0.899				
$J=1$	d_5	Ne	1.397	1.391	1.383				
		A	1.467	1.400	1.283			JJ	1.333
		Kr	1.098	1.348	1.355	1.294	1.208	Int.	1.067
		Xe	1.395		1.273	1.180	1.217		1.308
$J=2$	d_1''	Ne	0.948	0.990					
		A	0.908	0.941	1.107			JJ	1.121
		Kr		1.006	0.965	0.954	1.005	Int.	0.978
		Xe			1.073	0.987	0.980		
$J=2$	d_3	Ne	1.356	1.322	1.298				
		A	1.437	1.387	1.206			JJ	1.067
		Kr		1.295	1.318	1.315		Int.	1.300
		Xe	1.376	1.196?	1.303	1.298			
$J=2$	s_1''	Ne	1.242	1.230	1.251				
		A	0.987	1.265	1.264			JJ	1.289
		Kr	0.899					Int.	1.300
$J=2$	s_1''''	Ne	0.781	0.783					
		A	1.057	0.802	0.777			JJ	0.767
		Kr	1.169					Int.	0.756
		Xe	1.274*						
$J=3$	d_4	Ne	1.034	1.040	1.093				
		A		1.077	1.076	1.052		JJ	1.068
		Kr		1.050	1.073	1.094	1.037	Int.	1.036
		Xe		1.026	1.076	1.078	1.081		1.082
$J=3$	d_1'	Ne	1.249	1.248					
		A			1.199	1.245		JJ	1.237
		Kr		1.243	1.254	1.231	1.227	Int.	1.270
		Xe		1.263	1.246	1.225			
$J=3$	s_1'''	Ne	1.125	1.116					
		A		1.133	1.127	1.098		JJ	1.111
		Kr		1.140				Int.	1.111
		Xe	1.126						

* Should probably be labelled s_1''.

previous paper.[7] Excellent agreement is seen to exist between calculation and experiment. In the case of $5Y$, $5X$ the theoretical g values are 1.10 and 0.50. The values calculated from the pattern are 1.11 and 0.50. The difference between the observed and theoretical g value of the $5Y$ level can be accounted for by the fact that the $5Y$ and $5X$ levels are separated by 3.6 cm^{-1} instead of falling on top of each other. (See Fig. 1.)

With respect to the V, U ($3b'$, $2a'$) interaction, a serious discrepancy must be noted. Although the g values fit the theoretical calculations extremely well, the magnetic levels should not perturb each other very much because the interaction to be expected in this case almost cancels out. Yet the observed patterns are materially perturbed, and enough so to be somewhat greater than experimental error. Either the theory described here is too simple to be used in this particular case, or some perturbations from outside configurations are at work.

Table V gives a summary of the available data on the g factors of the rare gases for p^5p.

The tendency toward the limit for intermediate coupling is particularly evident for p_{10}.

Table VI gives a summary of the data for p^5d configurations.

Table VII gives the summary of experimental data for p^5f configurations.

It is in this configuration that the evidence in favor of the particular type of coupling assumed in this paper is most striking.

TABLE VII. g values for p^5f configurations of the rare gases.

						JJ	Int.
$J=1$	X	Kr	0.50	0.61*		0.500	0.500
$J=1$	X	Xe	0.504	0.50	0.50	0.500	0.500
$J=2$	V	Xe	0.86	0.87	0.87	1.047	0.844
$J=2$	Y	Xe	1.11	1.10	1.09	0.897	1.100
$J=3$	U	Xe	1.18	1.17		0.997	1.175
$J=4$	W_4	Xe	1.19			1.181	1.195
$J=4$	Z	Xe	1.02			1.034	1.022

* Perturbed by $4p^56p$.

[7] J. B. Green, Phys. Rev. **59**, 69 (1941).

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The Electric Breakdown and Cumulative Ionization

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Owing to cumulative ionization, in calculating the balance between the impact ionization and the recombination in a homogeneous electric field, three possible equilibrium values for the number of free electrons are obtained. It results in an S-like current *vs.* field strength curve. The breakdown is interpreted as an abrupt transition from the lower branch of the curve to the upper one. An expression for the breakdown field strength is obtained. It turns out to be of the correct order of magnitude. In a certain region of current densities, no stable homogeneous solutions exist, and the current is concentrated in the shape of a narrow discharge canal—a positive column. A non-linear differential equation for the distribution of free electrons in its cross section is obtained.

1.

IN considering the electric current through a gas in a homogeneous field, at not very low pressure and at sufficiently great distance between the electrodes, the boundary regions and those in the vicinity of the electrodes may be neglected. The number of free electrons obtained as a result of impact ionization is determined in this case by the equilibrium between ionization and recombination at every point:

$$\alpha n N = \rho n^2. \tag{1}$$

Here n stands for the estimated number of free electrons per unit volume; N is the number of gas molecules; α is the ionization coefficient; ρ—that of recombination. The number of positive ions is supposed not to differ essentially from the number of free electrons.

At any given field α and ρ have definite values, and Eq. (1) gives a definite value of n which increases with increasing field strength. Because of this increase in n, the current also increases continuously.

In reality, however, a continuous increase of the current proceeds only up to a certain value of the field, while at the further increase of the field, an abrupt change of the current takes place, that is, breakdown or the ignition of the gas discharge. Such an abrupt change may be obtained, if the cumulative ionization, that is the impact ionization of molecules, previously excited by the electron impact is taken into account in Eq. (1).

For the sake of simplicity we shall draw our attention only to two excited levels (1 and 2) between the ground level of the electron in a molecule (0) and the continuous spectrum. Let us denote the number of excited molecules per unit volume by n_1 and n_2, respectively. Usually $n \ll n_2 \ll n_1$, and in the approximate evaluation of n_1 the transitions to higher levels may be neglected. This gives

$$\beta_{01} n N = (\gamma_1 + \delta_1 n) n_1. \tag{2a}$$

Here β_{01} is the probability of collision of second kind between the excited molecule and the free electron.

In a similar way for the second level, if we neglect the ionization,

$$(\beta_{02} N + \beta_{12} n_1) n = (\gamma_2 + \delta_2 n) n_2, \tag{2b}$$

where β_{12} is the probability of secondary excitation $1 \rightarrow 2$, all the other designations are similar to those of Eq. (2a). Finally, for the number of collisions leading to ionization:

$$(\alpha_0 N + \alpha_1 n_1 + \alpha_2 n_2) n = \rho n^2. \tag{2c}$$

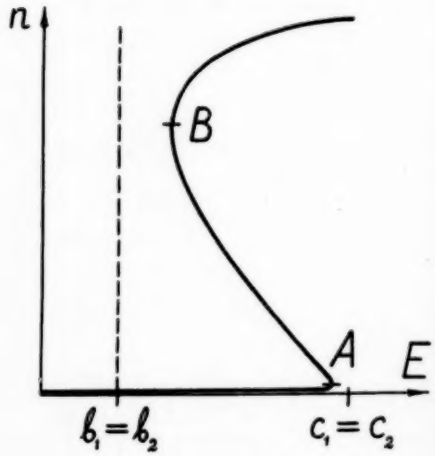

FIG. 1. Characteristic curve.

Here α_i is the probability of the ionization of the molecule in the ith excited state. Equations (2) give for n:

$$an^3+(b_1-b_2)n^2+(c_1-c_2)n-d=0, \quad (3)$$

where

$$a=\rho\delta_1\delta_2, \quad b_1=\rho(\gamma_1\delta_2+\gamma_2\delta_1), \quad c_1=\rho\gamma_1\gamma_2; \quad (4)$$

$$b_2=(\alpha_0\delta_1\delta_2+\beta_{01}\alpha_1\delta_2+\beta_{02}\alpha_2\delta_1+\beta_{01}\beta_{12}\alpha_2)N,$$

$$c_2=[\alpha_0(\gamma_1\delta_2+\gamma_2\delta_1)+\beta_{01}\alpha_1\gamma_2+\beta_{02}\alpha_2\gamma_1]N, \quad (5)$$

$$d=\alpha_0\gamma_1\gamma_2.$$

The number of free electrons capable of ionizing and exciting increases rapidly with the increase of strength of the applied field E. In a simplest case, when the mean free path of the electrons does not depend on their velocity, this number is proportional to[1]

$$f\sim\exp\left(-C\frac{\epsilon_i^2}{e^2E^2l^2}\right), \quad (6)$$

where ϵ_i is the energy of excitation or of ionization, respectively, l is the mean free path of the electrons; $C\ll1$. The coefficients α_i and β_{ik} must depend on the field strength approximately in the same way, and in comparison to the sharp exponential dependence, γ_i and δ_i may be considered independent of the field. Consequently a, b_1, and c_1 also do not depend on the field, while b_2, c_2, and d in weak fields are very small ($b_2\ll b_1$ and $c_2\ll c_1$) and increase strongly with the increase of the field strength.

The shape of the curve $n=n(E)$ according to Eq. (3) depends on the behavior of the coefficients of this equation. If c_2, increasing with the increase of the field strength, reaches the value of c_1 before b_2 reaches the value of b_1, then a monotonously increasing curve results. If, however, $b_2=b_1$ already at $c_2<c_1$, then an S-like curve is obtained (Fig. 1).

In reality, because of the fact that the distribution of the velocities of electrons in a homogeneous field decreases at a greater rate than the Maxwell distribution, the second case takes place. Thus, with the dependence prescribed by Eq. (6) we get

$$b_2\approx(\alpha_1\delta_2+\beta_{12}\alpha_2)\beta_{01}N, \quad c_2\approx\beta_{01}\alpha_1\gamma_2N. \quad (5')$$

In c_2 we have neglected $\beta_{02}\alpha_2\gamma_1$ in comparison with $\beta_{01}\alpha_1\gamma_2$. Usually $\epsilon_{01}>\epsilon_1$ and, due to this the exponential factor in the first of these quantities, is smaller than in the second. Now, by the order of magnitude

$$\alpha_1\delta_2\beta_{01}N/b_1\sim c_2/c_1,$$

but

$$\beta_{12}\alpha_2/\alpha_1\delta_2\sim\exp\left(2C\frac{\epsilon_{12}\epsilon_2}{e^2E^2l^2}\right);$$

consequently at $b_1=b_2$, $c_1>c_2$.

The solution of the Eq. (3) may be approximately substituted for by the solution of the square equations. At small n, neglecting the term with n^3, we get

$$n=\frac{1}{2(b_1-b_2)}\{c_2-c_1 \pm[(c_1-c_2)^2+4d(b_2-b_1)]^{\frac{1}{2}}\}. \quad (7)$$

The lower sign before the square root gives the first lower branch of the curve, the upper, the second branch. Both of the branches join at a point A (Fig. 1), when the expression under the square root disappears, and this gives the lower turn of the S-like characteristic.

At large values of n, d in Eq. (3) may be neglected. Then

$$n=\frac{1}{2a}\{b_2-b_1\pm[(b_2-b_1)^2+4a(c_2-c_1)]^{\frac{1}{2}}\}. \quad (8)$$

For the middle of the second branch, Eqs. (7) and (8) give approximately the same value:

$$n\approx(c_1-c_2)/(b_2-b_1).$$

If we increase the applied field strength, moving along the lower branch of the curve, then at a point A or close to it, an abrupt transition to the upper third branch—a breakdown or an ignition—should take place. We get the condition for the breakdown potential:

$$(c_1-c_2)^2=4d(b_2-b_1) \quad (9)$$

or approximately

$$c_2=c_1. \quad (9')$$

According to Eqs. (4) and (5') this gives

$$\alpha_1\beta_{01}N=\rho\gamma_1. \quad (10)$$

[1] M. J. Druyvesteyn, Physica **10**, 61 (1930); **1**, 1003 (1934); **3**, 65 (1936). B. Davydov, Physik. Zeits. Sowjetunion **8**, 59 (1935); **9**, 433 (1936). P. M. Morse, W. P. Allis, and E. S. Lamar, Phys. Rev. **48**, 412 (1935).

With known approximate values of the quantities involved, this gives the correct order of magnitude of the breakdown field.

If we take into account not only the two excited levels, as was done above, but a greater number of them, then in the same way, instead of Eq. (3), an equation of a higher degree should be obtained. However, for small values of n and for the region close to the lower turn of the characteristic, we may also in this equation neglect the higher powers of n, as we neglect the term with n^3 in solving Eq. (3). Because of this, the curve $n(E)$ at small values of n does not change essentially. Conditions (9) and (10) for the breakdown field shall particularly remain valid. By the way, even the second level does not enter Eq. (10), despite the fact that it is necessary in obtaining the turn of the curve.

Equation (10) is in an approximate agreement with the Paschen's law. Indeed, all the coefficients α_i and β_{ik} depend only on the product El [compare Eq. (6)], i.e., only on pd, where p is the gas pressure, d is the distance between the electrodes. The fact that p appears in Eq. (10) also through N cannot have any noticeable effect, since the dependence of ρ and α_i on β_{ik} is much stronger.

2.

The second middle branch of the characteristic is not stable. In Fig. 1, to the right of the curve, i.e., above the second branch, ionization overweighs the recombination. To the left, i.e., below the second branch, recombination overweighs. Because of this, close to the second branch, random deviations of n from the value prescribed by Eq. (3) shall not only not disappear, but, on the opposite, shall increase with time. Having included in series with a gas gap a very large constant resistance, it is always possible to fix not the field strength but practically the current intensity. The instability of the second branch of the characteristic leads to the fact that in the region of currents corresponding to n lying within the range from point A to point B no stable homogeneous states exist. Random fluctuations lead to the concentration of the current in the form of a narrow discharge canal—a positive column—in full accordance with the phenomena observed.

The existing theory of the positive column[2] does not take into consideration the cumulative ionization. It may be taken into account, if Eq. (3) is complemented by the diffusion terms. Because of the high concentration of the free electrons in the positive column, there exists a Maxwellian distribution of their velocities with an abnormally high temperature of the electrons, which depends on the longitudinal field. In this case, in the radial direction a quasi-neutral diffusion of electrons and positive ions with the ambipolar coefficients of the diffusion

$$D_a=\frac{k}{e}(T_-+T_+)\frac{u_-u_+}{u_-+u_+}\approx\frac{u_+kT_-}{e} \qquad (11)$$

is obtained. Here $u_\mp$ and $T_\mp$ are the mobilities and the temperatures of the free electrons and the positive ions, respectively.

Now in Eq. (3), to the decrease of the number of free electrons due to the recombination, we must add their decrease as a consequence of the ambipolar diffusion, i.e., we must make a substitution:

$$\rho n^2\rightarrow\rho n^2-\frac{D_a}{z}\frac{d}{dz}\left(z\frac{dn}{dz}\right).$$

This leads to the non-linear differential equation

$$(an^2+b_1n+c_1)\left[n-\frac{D_a}{\rho n}\left(\frac{d^2n}{dz^2}+\frac{1}{z}\frac{dn}{dz}\right)\right]=b_2n^2+c_2n+d. \qquad (12)$$

Outside of the discharge canal, estimated solutions of this equation must coincide with n_1, i.e., with the first root of Eq. (3) (Eq. (7) with the lower sign before the root sign):

With

$$z\rightarrow\infty,\quad n\rightarrow n_1.$$

On the other hand, the boundary condition at $z=0$ will be $dn/dz=0$. Here $n(0)$ itself must lie between the second and the third root of Eq. (3).

This sort of stable solutions of Eq. (12) must fill also the region of the current densities corresponding to the interval between the points A and B.

A more detailed account of this work will be published in the *Journal of Physics* U.S.S.R.

[2] W. Schottky, Physik. Zeits. **25**, 342 and 635 (1924); L. Tonks and I. Langmuir, Phys. Rev. **34**, 876 (1929).

The Propagation of Order in Crystal Lattices*

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Zernike's problem of the propagation of order in a binary crystal alloy is discussed by means of the matrix formalism recently developed for treating cooperative phenomena. It is proved generally that the existence of long range order over any temperature range implies a degeneracy of the maximum characteristic value of the fundamental matrix over the same temperature range. For a two-dimensional crystal, the special form of the matrix theory developed by Kramers and Wannier has been used to obtain explicitly the probabilities for finding an A or B atom at any lattice site if it is known that there is an A (or B) atom at a certain site (correlation probabilities, or intermediate range order). The results are obtained in the form of power series valid at low temperatures by a perturbation treatment of the highest characteristic values and characteristic vectors. It is seen that the maximum characteristic value is doubly degenerate from $T=0$ to some finite temperature, consistent with the existence of long range order at low temperature. The absence of long range order at high temperatures is proved by showing that the maximum characteristic value is non-degenerate at sufficiently high temperatures. By comparing the solutions of Zernike's approximate equations for the correlation probabilities in two dimensions with our exact solution, and his expressions for the long range order and energy (short range order) in three dimensions with those given by van der Waerden, we find that Zernike's approximation is better for a two- than a three-dimensional crystal. The problem of propagation of order is generalized by an investigation of the correlation probabilities for more complicated configurations of fixed atoms. For example, the ordering influence of an adjacent pair of disordered atoms ("dipole") is found as a function of position in the lattice. It is found here, as might be expected, that the ordering influence falls off rapidly with the distance of the site from the dipole. Other cases are treated as well.

IN order to interpret the diffuse scattering of x-rays by a partially disordered crystal alloy it is necessary to know how the presence of one atom at a certain lattice point affects the probability of finding the various kinds of atoms at the other lattice points. The older theories of the order-disorder problem, principally those of Bragg and Williams,[1] and Bethe,[2] gave only the long and short range order and did not consider the more general problem of finding the correlation proabilities for *all* distances, intermediate as well as long and short. Experimentally, several of these correlation probabilities were measured by Wilchinsky[3] for the alloy Cu_3Au, while the problem of calculating them theoretically was first attacked by Zernike[4] in a paper entitled "The Propagation of Order in Cooperative Phenomena."

In Zernike's work, the propagation of order is described by a partial finite difference equation relating the probability of finding a certain kind of atom at a given lattice point with the probabilities for various atoms at the nearest neighboring lattice points. However, his equation is necessarily approximate because in order to obtain a recurrence relation, he has to treat the probabilities for the nearest neighboring atoms as at least formally independent of one another. Nevertheless, this method is so far the only really practicable one for the three-dimensional propagation problem and gives reasonable results for the thermal properties and the correlation probabilities at low and high temperatures. One of the results of the present investigation will be to obtain a comparison in two dimensions between Zernike's solution and the exact solution valid at low temperatures. In three dimensions, exact series expansions for the long range order and the energy at low temperatures have been given by van der Waerden[5] and have been compared with the series of Zernike. The comparison indicates that Zernike's approximation is better in two dimensions than it is in three. In one dimension Zernike's solution can be shown to be exact. It therefore appears that the approximation

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[1] W. L. Bragg and E. J. Williams Proc. Roy Soc. London **145A**, 699 (1934).

[2] H. A. Bethe, Proc. Roy Soc. **150A**, 552 (1935).

[3] Z. W. Wilchinsky, Phys. Rev. **63**, 223 (1943).

[4] F. Zernike, Physica **7**, 565 (1940).

[5] v. d. Waerden, Zeits. f. Physik **118**, 473 (1941).

becomes successively poorer as the dimension is increased.

Although there was no further work directly following up that of Zernike, a new technique has been introduced into the study of the order-disorder phenomenon which shows some promise of providing a solution to the propagation problem. Recent work by Montroll,[6] Kramers and Wannier,[7] Lassettre and Howe,[8] and Onsager,[9] has shown how the statistical treatment of binary alloys can in principle be reduced to the solution of the characteristic value problem of a certain matrix, the characteristic values being related to the partition function for the crystal and the characteristic vectors to the probability for finding various configurations of the atoms in the lattice. It is the object of this paper to show how these matrix methods can be used to give at least a partial solution to the propagation problem.

The application of the matrix theory to real three-dimensional crystals has been held up unfortunately by considerable mathematical difficulties. The matrix whose characteristic value problem is to be solved is very difficult to handle even by perturbation methods, the essential complication arising from the fact that all its elements are different from zero and do not appear to vary in any regular manner from one position in the matrix to the next. These difficulties have so far compelled us to restrict our investigations to two-dimensional crystals, where the general matrix theory has been developed by Kramers and Wannier in a more tractable form. Using a perturbation method, valid at low temperatures, we have obtained power series for the maximum characteristic value and for the corresponding characteristic vectors. By inserting these series into the appropriate formalism of the matrix theory we then discuss the propagation problem by giving the correlation probabilities as functions of temperature and position in the lattice, obtaining series for the long range order, the short range order, and the order of intermediate range. The treatment is restricted to low temperatures, however, the perturbation theory at high temperatures being very complicated and difficult to carry through.

The paper is divided into two parts. Part I gives a brief outline of the matrix theory in three dimensions and contains a simple demonstration of the fact that states of long range order are not possible over a range of temperatures unless the maximum characteristic value of the associated matrix is degenerate over this same range. Part II is devoted to the discussion of the propagation problem in two-dimensional crystals.

I. LONG RANGE ORDER AND THE MATRIX METHOD

1. Results of the General Matrix Theory in Three Dimensions

In this section we shall collect the results of the general matrix theory which are applicable to the problem under consideration. The notation is identical with that used by Montroll.[6]

Consider a binary substitutional alloy AB whose crystal form is simple cubic. Let the edges of the crystal be L, M, N in units of the lattice distance. The crystal can then be regarded as made up of L layers of $M\times N$ atoms each, with each layer capable of 2^{MN} distinct configurations, corresponding to the fact that each of the $M\times N$ sites in the layer can be occupied by an A or a B atom. With the symbol α_j used for a typical one of the configurations available to the atoms in the jth layer, $v(\alpha_j)$ is to represent the total potential energy of interaction between all the nearest neighboring atoms of the jth layer in configuration α_j, and $v(\alpha_j, \alpha_{j+1})$ is taken as the representative of the total energy of interaction between atoms in the jth layer in configuration α_j with their nearest neighboring atoms in the $(j+1)$th layer in configuration α_{j+1}. With this notation and with the periodic boundary conditions imposed by requiring layer 1 to interact with layer L,[10] the partition function has the form,

$$Z=\sum_{\{\alpha_1\}}\cdots\sum_{\{\alpha_L\}}\exp-\{v(\alpha_1)+\cdots+v(\alpha_L)+v(\alpha_1,\alpha_2)+\cdots+v(\alpha_{L-1},\alpha_L)+v(\alpha_L,\alpha_1)\}/kT. \quad (1.1)$$

[6] E. W. Montroll, J. Chem. Phys. 9, 706 (1941).
[7] H. A. Kramers and G. H. Wannier, Phys. Rev. 60, 252 (1941).
[8] E. N. Lassettre and J. P. Howe, J. Chem. Phys. 9, 747 (1941); and 9, 801 (1941).
[9] Onsager's work is not yet published. He has, among other things, obtained a closed expression for the partition function of the two-dimensional lattice.

[10] This restriction is not necessary, serving merely to simplify the final formulae.

Making the substitution

$$V(\alpha_i, \alpha_j) = \tfrac{1}{2}v(\alpha_i) + v(\alpha_i, \alpha_j) + \tfrac{1}{2}v(\alpha_j),$$

we find that (1.1) becomes

$$Z = \sum_{\{\alpha_1\}} \cdots \sum_{\{\alpha_L\}} \left\{ \prod_{i=1}^{L} \exp\left(-V(\alpha_i, \alpha_{i+1})/kT\right) \right\}, \quad (1.2)$$

with the understanding that

$$\alpha_{L+1} \equiv \alpha_1.$$

Writing

$$\mathfrak{M}(\alpha, \alpha') = \exp\left[-V(\alpha, \alpha')/kT\right] \quad (1.3)$$

we define a symmetrical matrix $\mathfrak{M}$ whose $2^{MN} \times 2^{MN}$ rows and columns are labeled by $\alpha, \alpha', \alpha'', \cdots$ in accordance with the 2^{MN} possible configurations α. The characteristic values λ_r and characteristic vectors ψ_r $(r = 1, 2, \cdots, 2^{MN})$ of this matrix $\mathfrak{M}$ are fundamental for the theory. For, as we shall see, if we can solve the characteristic value problem

$$\mathfrak{M}\psi = \lambda\psi, \quad (1.4)$$

we shall have the answer to all questions of thermodynamic and statistical interest for the crystal, including the order-disorder phenomenon.

A characteristic vector ψ_r has 2^{MN} components, $\psi_r(\alpha)$, one for each configuration α. If we assume the λ_r and $\psi_r(\alpha)$ are known, the matrix element (3) can be written as

$$\exp\left[-V(\alpha, \alpha')/kT\right] = \sum_{r=1}^{2^{MN}} \lambda_r \psi_r(\alpha) \psi_r(\alpha'), \quad (1.5)$$

provided that the ψ_r are normalized to unity;

$$\textstyle\sum_\alpha \psi_r(\alpha)\psi_s(\alpha) = \delta_{rs}. \quad (1.6)$$

Substituting (1.5) into (1.2) and applying (1.6) one can easily prove that

$$Z = \sum_{r=1}^{2^{MN}} \lambda_r{}^L. \quad (1.7)$$

Thus the evaluation of Z, and consequently the investigation of thermodynamic quantities like entropy, energy, and specific heat, are reduced to the characteristic value problem (1.4). Since the number of layers L is very large for an actual crystal, the problem (1.4) can be restricted to that of obtaining the highest characteristic value λ_{max} and its corresponding characteristic vectors. If λ_{max} is d-fold degenerate[11] (1.7) becomes[12]

$$Z = d \cdot \lambda_{max}^{L}. \quad (1.8)$$

In the work of Montroll, and Kramers and Wannier it was assumed that λ_{max} was non-degenerate for all temperatures with the exception of possible isolated points. It was first pointed out by Lassettre and Howe[8] in their papers on binary solid solutions, that the maximum characteristic value is actually doubly degenerate for a range of temperatures beginning at $T = 0$, and they were able to demonstrate that within this range, a separation into two phases takes place. In the next section we shall show directly that this degeneracy of λ_{max} is a necessary condition for the existence of long range order.

2. Long Range Order and the Degeneracy of λ_{max}

Suppose that a state of long range order exists in the AB alloy and that it is known that the atoms in layer 1 have a certain configuration α_1. Then the probability for finding the atoms of layer n, very far from layer 1, in a certain configuration α_n, should depend explicitly on the configuration α_1. We shall show that if λ_{max} is non-degenerate, the probability for the configuration α_n is entirely independent of what configuration exists in layer 1, so that the non-degeneracy of λ_{max} will imply the absence of long range order.

The probability $P(\alpha_1, \alpha_n)$ of finding simultaneously the configuration α_1 in layer 1 and α_n in layer n, is given by an expression similar to (1.2) where, however, the configurations α_1 and α_n of layers 1 and n are held fixed. Using (1.5),

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[11] Although λ_{max} itself may not be degenerate, there may exist other characteristic values λ whose negatives are equal to λ_{max}. As is proved for a special case in part II, L will be even under such circumstances. A formula identical with (1.8) will then apply with d having an obvious meaning. In the future a statement that λ_{max} is degenerate will be understood to include the possibility mentioned here.

[12] It must be assumed here that the sum of the Lth powers of the remaining characteristic values is negligible compared with λ_{max}^{L}. Thus even if the ratios of the other characteristic values to λ_{max} are small, say less than $1-x$ with x close to unity, there are approximately 2^{MN} of them and there is no assurance that $2^{MN}(1-x)^{L}$ is small compared to unity.

(1.6), and (1.7) we find

$$P(\alpha_1, \alpha_n) = \frac{1}{\sum_r \lambda_r{}^L} \sum_{s=1}^{2^{MN}} \sum_{t=1}^{2^{MN}} \lambda_s{}^{n-1} \lambda_t{}^{L-n+1} \times \psi_s(\alpha_1)\psi_s(\alpha_n)\psi_t(\alpha_n)\psi_t(\alpha_1). \quad (2.1)$$

To discuss the long range order, n and $L-n$ must be taken as very large integers, the latter condition being necessary because of the boundary condition that layers 1 and L interact. This permits us to neglect all the characteristic values with the exception of $\lambda_{\max}$, and if the latter is assumed to be non-degenerate, (2.1) reduces to

$$P(\alpha_1, \alpha_n) = \psi_{\max}(\alpha_1)^2 \cdot \psi_{\max}(\alpha_n)^2. \quad (2.2)$$

If $P(\alpha_1, \alpha_n)$ is summed over all possible configurations α_n, we obtain the probability $P(\alpha_1)$ for finding layer 1 in configuration α_1. Since $\psi_{\max}$ is normalized to unity, this summation gives $P(\alpha_1) = \psi_{\max}(\alpha_1)^2$. Similarly, $P(\alpha_n) = \psi_{\max}(\alpha_n)^2$. Thus $P(\alpha_1, \alpha_n) = P(\alpha_1) \cdot P(\alpha_n)$. The probability for finding the configuration α_n when it is known that the atoms of layer 1 are in configuration α_1, is equal to $P(\alpha_1, \alpha_n)$ divided by $P(\alpha_1)$. This quotient is completely independent of α_1, being just equal to the probability for finding α_n when no restrictions at all are put on the other layers. There is therefore no long range order under these circumstances.

A further remark[13] concerning the interpretation of this result must be made, in the light of a theorem of Frobenius to the effect that if all the elements of a matrix are positive, the maximum characteristic value is likewise positive and in addition is non-degenerate. The elements of the matrix $\mathfrak{M}$, namely, $\exp[-V(\alpha, \alpha')/kT]$, are all greater than zero and will evidently remain bounded away from zero so long as M and N remain finite. Consequently, for any crystal in which the dimension L is very large compared with the dimensions M and N, $\lambda_{\max}^L$ will exceed by far the Lth power of any other characteristic value and states of long range order will not exist. On the other hand, if at least one of M and N is very large, and comparable to L in magnitude, it may happen that some of the matrix elements of $\mathfrak{M}$ are close enough to zero to cause a practical, if not actual, degeneracy in $\lambda_{\max}$; that is, there may exist other characteristic values λ, whose Lth powers are not appreciably less than $\lambda_{\max}^L$. If $\lambda_{\max}$ is d-fold degenerate, (2.1) becomes

$$P(\alpha_1, \alpha_n) = \frac{1}{d} \sum_{s=1}^{d} \sum_{t=1}^{d} \psi_{\max,s}(\alpha_1)\psi_{\max,s}(\alpha_n) \times \psi_{\max,t}(\alpha_n)\psi_{\max,t}(\alpha_1), \quad (2.3)$$

where the $\psi_{\max,s}$ are the characteristic vectors corresponding to $\lambda_{\max}$. Long range order will then in general be possible, since $P(\alpha_1, \alpha_n)$ no longer factors.

II. THE PROPAGATION OF ORDER IN TWO-DIMENSIONAL LATTICES

As was already pointed out in the introduction, the characteristic value problem (1.4) for three dimensions, is very difficult to handle. Therefore, in the hope of obtaining useful qualitative information which might possibly be carried over into three dimensions, we turn to the two-dimensional case where the corresponding problem is solvable. The matrix theory in two dimensions was developed mainly by Kramers and Wannier[7] in a paper on the statistics of two-dimensional ferromagnets.

In Section 3 we write down the matrix of Kramers and Wannier and review the properties of it which we shall find useful. Section 4 is devoted to a perturbation theory of the characteristic value problem, the main results of which are to show that the maximum characteristic value is doubly degenerate from $T=0$ to some finite temperature, and to obtain power series for the maximum characteristic value and the corresponding characteristic vectors valid at low temperatures. In the remaining sections, the solution is applied to various problems of physical interest. The long range order as a function of the temperature is obtained in Section 5, and in Section 6 a proof is given that an order-disorder transition actually occurs in the two-dimensional crystal. In Section 7 we discuss the general problem of the propagation of order through the lattice, showing in detail the gradual transition from the short range order to the influence at very great distances. In Section 8 Zernike's approximation is compared with the

[13] E. W. Montroll, J. Chem. Phys. 9, 711 (1941).

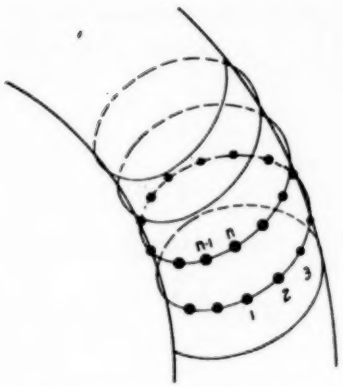

FIG. 1. A two-dimensional crystal on the surface of a torus.

exact solution. In Section 9, we treat the ordering influence of more complicated configurations of fixed atoms.

3. The Matrix of Kramers and Wannier

Kramers and Wannier have introduced a simplification into the theory of two-dimensional square lattices by making use of a special connectivity scheme for their crystal. This scheme can best be described as being equivalent to having the lattice sites regularly distributed along a continuous line twisting its way in screw-like fashion over the surface of a torus as in Fig. 1.

m pitches of n atoms each in this case take the place of L layers of $M\times N$ atoms each in the three-dimensional case. For convenience the atoms are distinguished by + and − instead of A and B, coordinates $\mu_1, \mu_2, \cdots, \mu_{mn}$ capable of assuming the values $+1$ and -1 being assigned to the respective lattice sites. The configuration of the atoms on a pitch will thus be given by a set of n values $(\mu_n\cdots\mu_2\mu_1)$. which we denote by α for brevity. In the magnetic case μ represents a spin capable of two orientations; for the case of alloys, the μ_j are still convenient for describing the various configurations. The energies of interaction between neighboring pairs are written $V(++)=V(--)=-\frac{1}{2}J$ and $V(+-)=\frac{1}{2}J$, so that the total energy is expressible as

$$E=-\tfrac{1}{2}J\sum\mu_i\mu_k, \tag{3.1}$$

where the sum is over all pairs of nearest neighbors. If J is positive, like atoms will attract one another and the ordered arrangement at low temperatures will be one in which the + and − atoms are separated into two phases. We shall then say that we are in the "ferromagnetic case." The "antiferromagnetic case," where J is negative, will lead to ordered states at low temperatures in which + and − atoms alternate on the lattice sites.

As in the three-dimensional case, a matrix $\mathfrak{M}$ is found whose characteristic value problem is fundamental for the statistical theory. $\mathfrak{M}$ has $2^n\times 2^n$ rows and columns labeled by the 2^n different possible configurations of the atoms on a pitch, $\alpha, \alpha', \alpha'', \cdots$. However, the matrix is not symmetrical, and it thus becomes necessary to introduce right- and left-handed characteristic vectors, say $\mathbf{A}_q$ and $\bar{\mathbf{B}}_p$, where

$$\mathfrak{M}\mathbf{A}_q=\lambda_q\mathbf{A}_q \quad\text{and}\quad \bar{\mathbf{B}}_p\mathfrak{M}=\lambda_p\bar{\mathbf{B}}_p. \tag{3.2}$$

With proper normalization the $\mathbf{A}_q$ and $\bar{\mathbf{B}}_p$ can be made to satisfy orthogonality conditions.

$$\bar{\mathbf{B}}_p\mathbf{A}_q=\textstyle\sum_\alpha \mathbf{B}_p(\alpha)\mathbf{A}_q(\alpha)=\delta_{pq}. \tag{3.3}$$

It actually turns out that the analogue of the matrix (1.3) in the three-dimensional case, is not $\mathfrak{M}$, but the nth power of $\mathfrak{M}$. Thus one finds, upon expressing the matrix element $(\alpha_1|\mathfrak{M}^n|\alpha_2)$ as a bilinear combination of the components $\mathbf{A}_q(\alpha_2)$ and $\mathbf{B}_q(\alpha_1)$.

$$\sum_{q=1}^{2^n}\lambda_q{}^n\mathbf{A}_q(\alpha_2)\mathbf{B}_q(\alpha_1)=\exp\left[-\frac{v(\alpha_2)+v(\alpha_1,\alpha_2)}{kT}\right], \tag{3.4}$$

where $v(\alpha_2)$ is the total energy of interaction between the nearest neighboring atoms of pitch 2 and $v(\alpha_1,\alpha_2)$ is the energy of interaction between the pitches 1 and 2. This relation, just as (1.5), plays a fundamental role.

By repeated use of (3.4) and (3.3) one finds for the partition function, the expression

$$Z=\sum_{p=1}^{2^n}\lambda_p{}^{mn} \tag{3.5}$$

and it appears, by comparison with (1.7), that λ^n is the analogue of the λ of the three-dimensional case. The advantage of this result of Kramers and Wannier is that now λ has a meaning which is independent of the size of the crystal, the logarithm of $\lambda_{\max}$ being essentially the free energy per particle. The variation of the properties of the crystal as it becomes infinite in two directions can therefore be studied conveniently by looking at $\lambda_{\max}$.

To write the matrix $\mathfrak{M}$ as a square array, it is necessary to arrange the 2^n configurations $\alpha=(\mu_n\cdots\mu_2\mu_1)$, in some definite order. The method chosen by Kramers and Wannier is the following: for any configuration, e.g., $++--+-+-$, one replaces every $+$ by a 0 and every $-$ by a 1 (giving in our example 00110010), reads the resulting number in the dual number system and takes that as the order number of the configuration. For the configuration above the order number is 50. It proves convenient to separate the configurations into two classes in accordance with the sign of μ_n. The configurations of the class $\mu_n=1$ consist of those with order numbers $0, 1, \cdots, 2^{n-1}-1$ and are arranged in that order. The remaining half of the configurations belong to the class $\mu_n=-1$ and are arranged in the order $2^n-1, 2^n-2, \cdots, 2^{n-1}$. The reason for the arrangement is the following. Configurations α and $\bar{\alpha}$ in corresponding places in the two classes have order numbers which add up to 2^n-1 and are conjugate to one another in the sense that α can be obtained from $\bar{\alpha}$ by changing every $+$ to a $-$ and vice versa.

Arranging the rows and columns to correspond to the arrangement of the configurations in the two classes, and introducing the new variable K and the functions α and β by

$$K=\frac{1}{2}\frac{J}{kT}, \quad \alpha=e^{2K}, \quad \beta=e^{-2K}$$

the matrix $\mathfrak{M}$ has the form

$$\mathfrak{M}(K)=\left\|\begin{array}{cccccc|cccccc}
\alpha 1 & & & & & & & & & & & \\
 & \alpha 1 & & & & & & & & & & \\
 & & \ddots & & & & & & & & & \\
 & & & \alpha 1 & & & & & & & 00 & \\
 & & & & 00 & & & & & & & \beta 1 \\
 & & & & & & & & & \iddots & & \\
 & & & & & & & & \beta 1 & & & \\
 & & & & & & & \beta 1 & & & & \\
\hline
 & & & & & & \alpha 1 & & & & & \\
 & & & & & & & \alpha 1 & & & & \\
 & & & & & & & & \ddots & & & \\
 & & & & 00 & & & & & & \alpha 1 & \\
 & & & & & \beta 1 & & & & & & 00 \\
 & & & & \iddots & & & & & & & \\
 & & & \beta 1 & & & & & & & & \\
\beta 1 & & & & & & & & & & &
\end{array}\right\|, \tag{3.6}$$

where blank spaces indicate zeros. $\mathfrak{M}(K)$ is easily seen to be reducible. Thus, with a matrix $\mathbf{H}$ defined by

$$\mathbf{H}=\frac{1}{\sqrt{2}}\left\|\begin{array}{c|c}\mathbf{I} & \mathbf{I}\\ \hline \mathbf{I} & -\mathbf{I}\end{array}\right\|. \tag{3.7}$$

$\mathbf{I}$ being the identity matrix of order 2^{n-1}, we have

$$\mathbf{H}\mathfrak{M}(K)\mathbf{H}^{-1}=\left\|\begin{array}{c|c}\mathbf{V}_+(K) & 0\\ \hline 0 & \mathbf{V}_-(K)\end{array}\right\|, \tag{3.8}$$

where

$$\mathbf{V}_+(K)=\left\|\begin{array}{cccccc}
\alpha 1 & & & & & \\
 & \alpha 1 & & & & \\
 & & \alpha 1 & & & \\
 & & & \ddots & & \\
 & & & & \alpha 1 & \\
 & & & & & \beta 1 \\
 & & & & \iddots & \\
 & & & \beta 1 & & \\
 & & \beta 1 & & & \\
\beta 1 & & & & &
\end{array}\right\|, \tag{3.9}$$

$$\mathbf{V}_-(K)=\left\|\begin{array}{cccccc}
\alpha & 1 & & & & \\
 & \alpha & 1 & & & \\
 & & \alpha & 1 & & \\
 & & & \ddots & & \\
 & & & & \alpha & 1 \\
 & & & & & -\beta-1 \\
 & & & & \iddots & \\
 & & & -\beta-1 & & \\
 & & -\beta-1 & & & \\
-\beta-1 & & & & &
\end{array}\right\|.$$

We shall call $\mathbf{V}_+(K)$ the "plus $\mathbf{V}$ matrix" and $\mathbf{V}_-(K)$ the "minus V matrix." The characteristic values and characteristic vectors of $\mathfrak{M}(K)$ fall into two classes. If $\psi_+(K)$ and $\psi_-(K)$ are right-handed characteristic vectors of $\mathbf{V}_+(K)$ and $\mathbf{V}_-(K)$, respectively, corresponding to the characteristic values $\lambda_+(K)$ and $\lambda_-(K)$, the associated characteristic vectors of $\mathfrak{M}(K)$ are

$$\mathbf{A}_+(K)=\mathbf{H}^{-1}\left\|\begin{array}{c}\psi_+(K)\\ \hline 0\end{array}\right\|=\left\|\begin{array}{c}\psi_+(K)\\ \hline \psi_+(K)\end{array}\right\|,$$

$$\mathbf{A}_-(K)=\mathbf{H}^{-1}\left\|\begin{array}{c}0\\ \hline \psi_-(K)\end{array}\right\|=\left\|\begin{array}{c}\psi_-(K)\\ \hline -\psi_-(K)\end{array}\right\|. \tag{3.10}$$

The components are arranged in the order of the two groups $\mu_n=1$ and $\mu_n=-1$. Similarly, if $\tilde{\phi}_+(K)$ and $\tilde{\phi}_-(K)$ are the left-handed characteristic vectors of $\mathbf{V}_+(K)$ and $\mathbf{V}_-(K)$, the corresponding vectors for $\mathfrak{M}(K)$ are

$$\tilde{\mathbf{B}}_+(K)=\|\tilde{\phi}_+(K),\ \tilde{\phi}_+(K)\|,$$
$$\tilde{\mathbf{B}}_-(K)=\|\tilde{\phi}_-(K),\ -\tilde{\phi}_-(K)\|. \tag{3.11}$$

As a final property of $\mathfrak{M}(K)$ which should be mentioned, there is a simple device by which one can treat the antiferromagnetic case once the ferromagnetic case has been discussed. In the former case, the interaction energy J is negative and the parameter K is therefore negative. In the ferromagnetic case, $K>0$. If $\mathbf{R}$ is a permutation matrix which changes every alternate atom on a pitch from + to − and vice versa, it is readily verified that

$$\mathbf{RH}\mathfrak{M}(-K)\mathbf{H}^{-1}\mathbf{R}^{-1}=\left\|\begin{array}{c|c}\mathbf{V}_+(K) & 0\\ \hline 0 & -\mathbf{V}_-(K)\end{array}\right\|, \tag{3.12}$$

so that the characteristic values of $\mathfrak{M}(-K)$ are $\lambda_+(K)$ and $-\lambda_-(K)$. The characteristic vectors $\mathbf{A}_+(-K)$, etc., are obtained from $\mathbf{A}_+(K)$, $\tilde{\mathbf{B}}_+(K)$, $\cdots$ by permuting the components according to $\mathbf{R}$.

The problem with which we are now faced is that of finding the characteristic values and characteristic vectors of the plus and minus $\mathbf{V}$ matrices as functions of the temperature. Kramers and Wannier have neglected the minus $\mathbf{V}$ matrix in their treatment, but this is unimportant for the discussion of the thermal properties. We are, however, interested in the degeneracy of λ_{max} and shall find in the next section that the maximum characteristic value of $\mathbf{V}_-$ is equal to the maximum characteristic value of $\mathbf{V}_+$ in the limiting case of an infinitely large crystal.

4. Solution of the Matrix Problem for Low Temperatures

For the low temperature ferromagnetic case, K is very large and positive, so that the parameter $\beta=e^{-2K}$ is very small, approaching 0 as the temperature tends to zero. It then becomes possible to carry out an expansion in powers of β. Thus, by defining a new matrix, $\mathbf{U}_+(\beta)$, the plus $\mathbf{V}$ matrix can be written

$$\mathbf{V}_+(K)=\alpha\begin{Vmatrix}1 & \beta & & & & \\ & 1 & \beta & & & \\ & & \ddots & & & \\ & & & 1 & \beta & \\ & & & & \beta^2 & \beta \\ & & & \beta^2 & & \\ \beta^2 & & & & & \end{Vmatrix}\equiv\frac{1}{\beta}\mathbf{U}_+(\beta). \tag{4.1}$$

$\mathbf{U}_+(\beta)$ can be expanded in the form

$$\mathbf{U}_+(\beta)=\begin{Vmatrix}1 & & & & \\ & 1 & & & \\ & & \ddots & & \\ & & & 1 & \\ & & & & 1\end{Vmatrix}+\beta\begin{Vmatrix}0 & 1 & & & \\ & 0 & 1 & & \\ & & \ddots & & \\ & & & 0 & 1 \\ 1 & & & & 0\end{Vmatrix}+\beta^2\begin{Vmatrix}0 & & & & 1 \\ & 0 & & & \\ & & \ddots & & \\ & & & 0 & \\ 1 & & & & 0\end{Vmatrix}. \tag{4.2}$$

Defining the constant matrices $\mathbf{U}_0$, $\mathbf{U}_1$, and $\mathbf{U}_2$ by (4.2) we may write for brevity

$$\mathbf{U}_+(\beta)=\mathbf{U}_0+\beta\mathbf{U}_1+\beta^2\mathbf{U}_2. \tag{4.3}$$

If there are n atoms per pitch, these matrices will have 2^{n-1} rows and columns corresponding to

the configurations 0, 1, 2, $\cdots$, $2^{n-1}-1$ which all have $\mu_n=1$.

Our procedure will consist in obtaining power series in the parameter β for the maximum characteristic value λ_{max} and corresponding characteristic vector ψ_{max} of the matrix $\mathbf{U}_+(\beta)$. It is evident that $\mathbf{U}_0$ has a single non-degenerate characteristic value of unity and a $2^{n-1}-1$-fold degenerate value of zero. Therefore, λ_{max} will be well separated from the other characteristic values at low temperatures and will be an analytic function of β in the neighborhood of $\beta=0$. One will thus be justified in trying series expansions for λ_{max} and ψ_{max} of the form

$$\begin{aligned}\lambda=\lambda_{max}&=\lambda_0+\beta\lambda_1+\beta^2\lambda_2+\cdots+\beta^p\lambda_p+\cdots,\\ \psi=\psi_{max}&=\psi_0+\beta\psi_1+\beta^2\psi_2+\cdots+\beta^p\psi_p+\cdots.\end{aligned}\tag{4.4}$$

Inserting (4.4) into the equation $\mathbf{U}_+(\beta)\psi=\lambda\psi$, and equating coefficients of like powers of β, we find a set of equations for the λ_p and ψ_p:

$$\begin{aligned}&0)\quad U_0\psi_0=\lambda_0\psi_0,\\ &1)\quad U_0\psi_1+U_1\psi_0=\lambda_0\psi_1+\lambda_1\psi_0,\\ &2)\quad U_0\psi_2+U_1\psi_1+U_2\psi_0=\lambda_0\psi_2+\lambda_1\psi_1+\lambda_2\psi_0,\\ &p)\quad U_0\psi_p+U_1\psi_{p-1}+U_2\psi_{p-2}=\sum_{q=0}^{p}\lambda_q\psi_{p-q},\quad p\geqq 3.\end{aligned}\tag{4.5}$$

The characteristic vector ψ_0 corresponding to $\lambda_0=1$ evidently has only one non-vanishing component, that corresponding to configuration number zero. We therefore take $\psi_0(0)=1$ and $\psi_0(\alpha)=0$ for $\alpha=1, 2, \cdots, 2^{n-1}-1$. Thus for ψ_0 and its adjoint vector, $\bar{\psi}_0$, we have

$$\psi_0=\begin{Vmatrix}1\\0\\\cdot\\\cdot\\\cdot\\0\end{Vmatrix},\quad \bar{\psi}_0=\|\,1\;0\;\cdots\;0\,\|.\tag{4.6}$$

Since $\mathbf{U}_1\psi_0\equiv 0$, the equation for ψ_1 and λ_1 is

$$\mathbf{U}_0\psi_1=\psi_1+\lambda_1\psi_0.$$

Taking the inner product on the left with the vector $\bar{\psi}_0$ and noticing that $\bar{\psi}_0\mathbf{U}_0=\psi_0$, we find that $\lambda_1=0$. The vector ψ_1 then satisfies the equation $\mathbf{U}_0\psi_1=\psi_1$. It is clear, however, that we are at liberty to choose ψ_1 and all the remaining ψ_p orthogonal to ψ_0, saving the final normalization of ψ until the end. With this restriction, ψ_1 must vanish identically.

Multiplying the equation for ψ_2 on the left by $\bar{\psi}_0$, we find in this case also that $\lambda_2=0$. To find ψ_2 we must therefore solve the equation

$$(\mathbf{I}-\mathbf{U}_0)\psi_2=\mathbf{U}_2\psi_0,$$

where $\mathbf{I}$ is the identity matrix.

Denoting the components of ψ_2 by $\psi(\alpha)$ ($\alpha=0, 1, 2, \cdots, 2^{n-1}-1$), we find for $(\mathbf{I}-\mathbf{U}_0)\psi_2$ and $\mathbf{U}_2\psi_0$ the vectors

$$(\mathbf{I}-\mathbf{U}_0)\psi=\begin{Vmatrix}0\\ \psi(1)-\psi(2)\\ \psi(2)-\psi(4)\\ \vdots\\ \psi(j)-\psi(2j)\\ \vdots\\ \psi(2^{n-2}-1)-\psi(2^{n-1}-2)\\ \psi(2^{n-2})\\ \vdots\\ \psi(2^{n-2}+p)\\ \vdots\\ \psi(2^{n-1}-1)\end{Vmatrix},\tag{4.7}$$

$$\mathbf{U}_2\psi_0=\begin{Vmatrix}0\\0\\\vdots\\0\\0\\\vdots\\0\\1\end{Vmatrix}.\tag{4.8}$$

Equation (4.7) is of the type $(\mathbf{I}-\mathbf{U}_0)\psi=\xi$, where ξ is a known vector and ψ is to be found. The entire perturbation procedure consists in repeatedly solving equations of this kind. The method used is the following. Since the components 2^{n-2}, $2^{n-2}+1$, $\cdots$, $2^{n-1}-1$ of $(\mathbf{I}-\mathbf{U}_0)\psi$ are identical with those of ψ, they are obtained immediately from the corresponding components of ξ. The remaining half of the components of ψ are obtained with the help of those already known. For example,

$$\psi(2^{n-2}-1)=\psi(2^{n-1}-2)+\xi(2^{n-2}-1),$$

$$\psi(2^{n-2}-2)=\psi(2^{n-1}-4)+\xi(2^{n-2}-2),$$

etc.

A component of even index j is coupled directly to the component of index $\frac{1}{2}j$ and indirectly to those with indices $\frac{1}{4}j$, $\frac{1}{8}j$ . . . if j is also divisible by 4, 8. . . . One continues to follow the even components $j/2^k$ until further division by 2 is no longer possible.

Applied to ψ_2, the procedure gives $\psi_2(2^{n-1}-1)=1$ and $\psi_2(\alpha)=0$ for $\alpha=0, 1, 2, \cdots, 2^{n-1}-2$. Multiplying the equation for ψ_3 on the left by $\tilde{\psi}_0$, we find $\lambda_3=\tilde{\psi}_0\mathbf{U}_1\psi_2$. In general, from the fact that ψ_0 is orthogonal to the other ψ_j and that $\tilde{\psi}_0\mathbf{U}_2=0$, we find $\lambda_r=\tilde{\psi}_0\mathbf{U}_1\psi_{r-1}$. However, since

$$\tilde{\psi}_0\mathbf{U}_1=\|0\ 1\ 0\ \cdots\ 0\|,$$

we have

$$\lambda_r=\psi_{r-1}(1). \tag{4.9}$$

Since the component number 1 of ψ_2 vanishes we see that $\lambda_3=0$. ψ_3 is then to be found from the equation $(\mathbf{I}-\mathbf{U}_0)\psi_3=U_1\psi_2$. The non-zero components of $\mathbf{U}_1\psi_2$ are

$$(\mathbf{U}_1\psi_2)(2^{n-2}-1)=1, \quad (\mathbf{U}_1\psi_2)(2^{n-2})=1.$$

The non-zero components of ψ_3 are therefore

$$\psi_3(2^{n-2})=1, \quad \psi_3(2^{n-2}-1)=1,$$
$$\psi_3(2^k)=1 \quad (k=1, 2, \cdots, n-3)$$

arising from the connection with the component 2^{n-2}, and $\psi_3(1)=1$ arising from the connection with $\psi_3(2)$.

From (4.9) we then find $\lambda_4=\psi_3(1)=1$. The vector ψ_4 therefore satisfies the equation

$$(\mathbf{I}-\mathbf{U}_0)\psi_4=\mathbf{U}_1\psi_3+\mathbf{U}_2\psi_2-\psi_0.$$

However, $\mathbf{U}_2\psi_0=0$. Since

$$(\mathbf{U}_1\psi)(j)=(\mathbf{U}_1\psi)(2^{n-1}-1-j)=\psi(2j+1),$$

we find for the non-vanishing components of $\mathbf{U}_1\psi_3$ the following:

$$(\mathbf{U}_1\psi_3)(0)=(\mathbf{U}_1\psi_3)(2^{n-1}-1)=1$$

and

$$(\mathbf{U}_1\psi_3)(2^{n-3}-1)=(\mathbf{U}_1\psi_3)(3.2^{n-3})=1.$$

Therefore,

$$\psi_4(2^{n-1}-1)=1, \quad \psi_4(3.2^{n-3})=1$$

and from this

$$\psi_4(3.2^k)=1 \quad (k=1\cdots n-4), \quad \psi_4(3)=1;$$

finally $\psi_4(2^{n-3}-1)=1$.

This perturbation procedure was carried as far as the 12th power of β and gives for the maximum characteristic value of the plus $\mathbf{V}$ matrix[14]

$$\lambda_+=\frac{1}{\beta}(1+\beta^4+2\beta^6+5\beta^8+14\beta^{10}+44\beta^{12}+\cdots). \tag{4.10}$$

The convergence of this series will be inferred later on. More complete series for ψ_+ will also be given later together with the characteristic vectors of the minus $\mathbf{V}$ matrix. However, up to terms of the order β^5, the non-zero components of the approximating vectors are given in Table I.

The expression (4.10) for λ_+, if carried out completely, would essentially give the free energy per particle for an infinite crystal (i.e., one for which $n=\infty$). For any finite crystal the corresponding series will agree with the limiting one, (4.10), up to a certain power of β, after which they will differ. It is not difficult to see from the perturbation procedure that the agreement will persist to higher and higher powers of β as n increases. The only reason for a difference between the limiting series and the one for finite n, is that at some stage in the calculation two or more components of a vector which are labeled differently actually become identical. For example, in the case $n=5$ the component number 3 of the fourth approximating vector ψ_4 does not have the value 1 as one would find by the above methods, but actually has the value 2. This comes about because the component labeled $2^{n-3}-1$ is also the component number 3. Because of these coincidences the components of the approximating vector ψ_r and hence also the coefficients λ_r for a given n, will eventually differ, as r increases, from the ψ_r and λ_r for larger values of n. However, these coincidences can be postponed by taking larger and larger values for n, so that at any fixed stage r in the approximation a given component of ψ_r or the value of λ_r will be the same for all sufficiently large finite problems.

The same type of perturbation procedure is applicable to the problem of the minus $\mathbf{V}$ matrix. Carried as far as terms of the order β^{12} we find that its maximum characteristic value λ_- is

[14] The terms up to β^{10} of this series were previously obtained by Bloch, using a different method. F. Bloch, Zeits. f. Physik 61, 206 (1930).

TABLE I. The approximating vectors ψ_0 to ψ_5.

ψ_0 Component	Value	ψ_2 Component	Value	ψ_3 Component	Value	ψ_4 Component	Value	ψ_5 Component	Value
0	1	$2^{n-1}-1$	1	1	1	3	1	1	2
				2^k $k=1\cdots n-3$	1	3.2^k $k=1\cdots n-4$	1	7	1
				$2^{n-2}-1$	1	$2^{n-3}-1$	1	2^k $k=1\cdots n-2$	1
				2^{n-2}	1	3.2^{n-3}	1	7.2^k $k=1\cdots n-4$	1
						$2^{n-1}-1$	1	$2^{n-4}-1$	1
								$2^{n-2}-1$	3
								$2^{n-1}-2^k-1$ $k=1\cdots n-3$	1
								$2^{n-1}-2$	2

identical with λ_+ for sufficiently large n. Moreover we find to this approximation that the components of the vector ψ_- are identical with those of ψ_+ except for characteristic differences in sign. For any finite value of n, the characteristic values λ_+ and λ_- will differ. However, experience with the perturbation method leads us to believe that as n becomes increasingly large, the difference between λ_+ and λ_- is postponed to higher and higher powers of β, so that in the limiting case of an infinite crystal the degeneracy between λ_+ and λ_- will be expected to hold as far as the series converge. Really to give a proof of the degeneracy, one would have to devise some inductive argument of the type given by Lassettre and Howe[15] to show the degeneracy of the maximum characteristic value of the matrix for the three-dimensional problem.

To find the left-handed characteristic vectors $\tilde{\mathbf{B}}_+$ and $\tilde{\mathbf{B}}_-$ the problems of obtaining the left-handed characteristic vectors of the plus and minus $\mathbf{V}$ matrices are treated by the same perturbation methods. The same series for λ_+ and λ_- are found as previously and the equality, except for characteristic sign differences, of the components of $\tilde{\boldsymbol{\phi}}_+$ and $\tilde{\boldsymbol{\phi}}_-$ is also observed.

For a proof of the convergence of the series for λ_+ and λ_- we refer to the work of van der Waerden.[5] By a consideration of the probabilities for finding polygons of various lengths enclosing atoms which are not ordered with respect to one another, he calculates the long range order and the energy of the crystal at low temperatures, obtaining series identical with ours. Although his method would be very cumbersome for treating the general propagation problem, it is more powerful than the matrix method in the respect that it provides simple convergence proofs. From the convergence of the series for the energy we can conclude that the series for λ_+ and λ_- also converge. The energy is obtained from the partition function, or from the partition function per particle, by

$$\begin{aligned} E &= -\frac{\partial \log Z}{\partial(1/kT)} = NJ\beta\frac{d\log\lambda_+}{d\beta} \\ &= -NJ+NJ\beta\frac{d\log(\beta\lambda_+)}{d\beta} \\ &= -NJ+NJ\{4\beta^4+12\beta^6+36\beta^8 \\ &\qquad +120\beta^{10}+448\beta^{12}+\cdots\}. \end{aligned} \tag{4.11}$$

This is the same as the series for the energy which is given by van der Waerden and from his proof of its convergence we see that the logarithmic derivative of $\beta\lambda_+$ is analytic in the neighborhood of $\beta=0$. The logarithm of $\beta\lambda_+$ is therefore analytic at $\beta=0$ and hence the same is true of $\beta\lambda_+$ itself.

5. The Long Range Order

The probability $P(\alpha_1, \alpha_r)$ of finding simultaneously pitch 1 in configuration α_1, and pitch r in configuration α_r is given by an expression analagous to (2.1) of Section 2. Using (3.3), (3.4), and (3.5) one finds

$$\begin{aligned} P(\alpha_1,\alpha_r) = \frac{1}{\sum_p \lambda_p{}^{mn}} \sum_p \sum_q \lambda_p{}^{(r-1)n}\lambda_q{}^{(m-r+1)n} \\ \times \mathbf{B}_p(\alpha_1)\mathbf{A}_q(\alpha_1)\mathbf{B}_q(\alpha_r)\mathbf{A}_p(\alpha_r). \end{aligned} \tag{5.1}$$

In the ferromagnetic case, for sufficiently low temperatures, we have found the maximum

[15] E. N. Lassettre and J. P. Howe, J. Chem. Phys. 9, 801 (1941).

characteristic value to be two-fold degenerate. Therefore, for two pitches far enough apart so that $r-1$ and $m-r+1$ are large integers, we have

$$P(\alpha_1, \alpha_r) = \tfrac{1}{2}\{\mathbf{B}_+(\alpha_1)\mathbf{A}_+(\alpha_r)+\mathbf{B}_-(\alpha_1)\mathbf{A}_-(\alpha_r)\} \times\{\mathbf{B}_+(\alpha_r)\mathbf{A}_+(\alpha_1)+\mathbf{B}_-(\alpha_r)\mathbf{A}_-(\alpha_1)\}. \quad (5.2)$$

Let us now ask for the probability of finding two + atoms simultaneously, one in a given position in pitch 1 and the other at a given place in pitch r. In particular we might ask that the two end atoms of the separate pitches be both +. Then the probability P in question is obtained by summing $P(\alpha_1, \alpha_r)$ over those configurations consistent with having + atoms at the end of the pitch. These comprise the first half of all the configurations, namely, the ones numbered from 0 to $2^{n-1}-1$.

From (3.10) and (3.11) the normalized forms of $\mathbf{A}_+$ and $\mathbf{B}_+$ are

$$\mathbf{A}_+ = (2\bar{\boldsymbol{\phi}}_+\psi_+)^{-\frac{1}{2}}\begin{Vmatrix}\psi_+\\ \psi_+\end{Vmatrix}, \qquad \mathbf{B}_+ = (2\bar{\boldsymbol{\phi}}_+\psi_+)^{-\frac{1}{2}}\|\bar{\boldsymbol{\phi}}_+, \bar{\boldsymbol{\phi}}_+\|. \quad (5.3)$$

In the same way, the normalizing factor for the minus vectors is $(2\bar{\boldsymbol{\phi}}_-\psi_-)^{-\frac{1}{2}}$. However, the series expansions show that $\bar{\boldsymbol{\phi}}_-\psi_- = \bar{\boldsymbol{\phi}}_+\psi_+$. It also turns out that $\mathbf{B}_+(\alpha)\mathbf{A}_+(\alpha)=\mathbf{B}_-(\alpha)\mathbf{A}_-(\alpha)$ and that $\mathbf{B}_+(\alpha)\mathbf{A}_-(\alpha)=\mathbf{B}_-(\alpha)\mathbf{A}_+(\alpha)$. Using these relations, multiplying out (5.2), and summing over the first half of the configurations, we obtain for P the expression

$$P=\tfrac{1}{4}\{1+(\bar{\boldsymbol{\phi}}_+\psi_-/\bar{\boldsymbol{\phi}}_+\psi_+)^2\}. \quad (5.4)$$

It can be verified without very much difficulty that this same expression remains valid if the two + atoms under consideration do not necessarily occupy corresponding positions in the two distant pitches. P is therefore the chance of finding simultaneously two + atoms very far apart in a ferromagnetic crystal. In the absence of long range order, $P=\frac{1}{4}$.

If the crystal is antiferromagnetic, this probability will of course depend on the odd or even character of the number of steps between the two atoms. Instead of a degeneracy in λ_{max}, we have, from (3.12), $\lambda_+(-K)=-\lambda_-(-K)$. The total number of atoms in the crystal, mn is even, however, since there are as many + atoms as − atoms. Thus, $\lambda_+(-K)^{mn}=\lambda_-(-K)^{mn}$, and the effect is the same as though there were a real degeneracy. Also, from (3.12), we see that the characteristic vectors $\bar{\boldsymbol{\phi}}_\pm(-K)$, $\psi_\pm(-K)$ are obtained from $\bar{\boldsymbol{\phi}}_\pm(K)$, $\psi_\pm(K)$ by permuting the components in accordance with a certain permutation matrix $\mathbf{R}$. The components of $\bar{\boldsymbol{\phi}}_\pm(K)$ and $\psi_\pm(K)$ are permuted in the same way, however. Consequently the inner products of the vectors are invariant; that is, for example,

$$\bar{\boldsymbol{\phi}}_+(K)\cdot\psi_-(K)=\bar{\boldsymbol{\phi}}_+(-K)\cdot\psi_-(-K)$$

and

$$\bar{\boldsymbol{\phi}}_+(K)\cdot\psi_+(K)=\bar{\boldsymbol{\phi}}_+(-K)\cdot\psi_+(-K).$$

Carrying out the computation for P, we find an expression

$$P=\tfrac{1}{4}\{1+(-1)^k(\bar{\boldsymbol{\phi}}_+\psi_-/\bar{\boldsymbol{\phi}}_+\psi_+)^2\}, \quad (5.5)$$

where k is, say, the smallest number of steps between the two + atoms entering into the definition of P. If k is even, the two + atoms form an ordered pair, and P exceeds $\frac{1}{4}$. If k is odd, the pair of + atoms is not ordered, and P is less than $\frac{1}{4}$.

To make connection with the usual long range order S we shall obtain an expression for P in terms of S and compare with (5.4) and (5.5). For an antiferromagnetic alloy, one divides the sites of the crystal into two groups, α and β sites, the former being occupied exclusively by + atoms at the zero of temperature and the latter by − atoms. At a finite temperature one denotes by r the probability that an atom be right, or on a site which is appropriate to it, and by w the probability that a + or a − atom be wrong, that is, be on a site not appropriate to it. The long range order S is then defined by writing w and r in the form

$$w=\tfrac{1}{2}(1-S), \quad r=\tfrac{1}{2}(1+S). \quad (5.6)$$

In terms of S, the probability, P, for finding two atoms, of which one is +, and which are correctly ordered with respect to one another is given by

$$P=\frac{1}{2}\left(\frac{1+S}{2}\right)^2+\frac{1}{2}\left(\frac{1-S}{2}\right)^2=\frac{1}{4}(1+S^2). \quad (5.7)$$

This can be seen as follows. If one takes the factors in order, the first $\frac{1}{2}$ is the chance that an α site is selected for the first atom of the pair, which we may take as $+$. The chance of getting a $+$ atom on this site and also of getting the right atom at the distant site, is then $\frac{1}{4}(1+S)^2$. If the site chosen originally is a β site, the two atoms of the pair would both have to be wrong from the point of view of the $\alpha-\beta$ sites in order to be correct with respect to one another. This would give the factor $\frac{1}{4}(1-S)^2$. In the same way the probability for finding two distant atoms which are not correctly ordered with respect to one another, is $\frac{1}{4}(1-S^2)$.

From (5.4) and (5.5) it therefore follows that the long range order S is given in terms of the characteristic vectors by

$$S=\tilde{\phi}_+\psi_-/\tilde{\phi}_+\psi_+. \tag{5.8}$$

The computation of S up to terms of order β^8 is given in Table II. All configurations α which give the same series expansion for $\phi_+(\alpha)\psi_-(\alpha)$, to terms of order β^8, are grouped together and listed in the first column. The number of configurations in each group is given in column two. The third column gives the coefficients of β^0, β^4, β^6, and β^8 appearing in the series for $\phi_+(\alpha)\psi_-(\alpha)$. To obtain $\tilde{\phi}_+\psi_-$, we must sum $\phi_+(\alpha)\psi_-(\alpha)$ over all α from 0 to $2^{n-1}-1$. This is conveniently done by multiplying the coefficients in the third column by the number of configurations in the second column and then adding. The results are indicated in the last column. We have

$$\tilde{\phi}_+\psi_-=1+(n-2)\beta^4+(3n-7)\beta^6+\left(\frac{1}{2}n^2+\frac{17}{2}n-30\right)\beta^8+\cdots. \tag{5.9a}$$

The product $\tilde{\phi}_+\psi_+$ is gotten in the same way. Its table differs from that of $\tilde{\phi}_+\psi_-$ only in that all the signs of the $\phi_+(\alpha)\psi_+(\alpha)$ are positive. Otherwise the numerical values are the same as for the $\phi_+(\alpha)\psi_-(\alpha)$. Making the appropriate changes we find

$$\tilde{\phi}_+\psi_+=1+n\beta^4+(3n+1)\beta^6+\left(\frac{1}{2}n^2+\frac{21}{2}n+4\right)\beta^8+\cdots. \tag{5.9b}$$

Both $\tilde{\phi}_+\psi_-$ and $\tilde{\phi}_+\psi_+$ depend on the size of the crystal, n, but their quotient, which is the long range order, must be independent of n for very large n. Performing the division, we obtain to terms of order β^{12}

$$S=\tilde{\phi}_+\psi_-/\tilde{\phi}_+\psi_+=1-2(\beta^4+4\beta^6+17\beta^8+76\beta^{10}+357\beta^{12}+\cdots) \tag{5.10}$$

and

$$P=\tfrac{1}{4}(1+S^2)=\tfrac{1}{2}-\beta^4-4\beta^6-16\beta^8-68\beta^{10}-307\beta^{12}-\cdots. \tag{5.11}$$

This same series for S was found by van der Waerden and a proof was given that it is convergent for $\beta<\frac{1}{3}$. The question of the actual radius of convergence of the series is still open, however. A highly probable conjecture can be made in the light of the investigations of Kramers and Wannier. On the basis of an important symmetry property of the plus **V** matrix, they are able to show that if it is assumed that the crystal can have only one point of singular behavior, that point must be given by

$$\beta_c=\sqrt{2}-1=0.414. \tag{5.12}$$

As we shall prove in the next section, there is no long range order at high temperatures. It therefore seems very probable that the point $\beta_c=0.414$ represents the Curie point for the transition from order to disorder and that the series for S has radius of convergence 0.414. A real proof of this fact and an investigation of the limiting value of $S(\beta)$ as β approaches β_c from below, would be very much desired, however.

6. Proof That an Order-Disorder Transition Actually Takes Place

Although the location of the transition point between states with finite long range order and those with no long range order has not been rigorously obtained by the matrix method, it is easy to give a proof that such a transition really occurs. Such proofs have been given by Peierls[16] and van der Waerden[5] using the properties of polygons enclosing regions of disordered atoms.

[16] R. Peierls, Proc. Camb. Phil. Soc. **32**, 477–481 (1936).

TABLE II. The calculation of $\bar{\phi}_+\bar{\psi}_-$.

Configuration, α		Number in group	$\phi_+(\alpha)\psi_-(\alpha)$ β^0	β^4	β^6	β^8	$\bar{\phi}_+\bar{\psi}_-$ β^0	β^4	β^6	β^8
0		1	1				1			
2^k	$k=1\cdots n-2$	$n-2$		1	2	5		$n-2$	$2n-4$	$5n-10$
3.2^k	$k=1\cdots n-3$	$n-3$			1	6			$n-3$	$6n-18$
2^j+2^k	$j=3\cdots n-2$, $k=1\cdots j-2$	$\frac{1}{2}(n-4)(n-3)$				1				$\frac{1}{2}n^2-\frac{7}{2}n+6$
7.2^k	$k=1\cdots n-4$	$n-4$				1				$n-4$
$2^{n-1}-2$		1				-4				-4
1		1		1	3	8		1	3	8
3		1			1	7			1	7
7		1				1				1
2^k+1	$k=2\cdots n-2$	$n-3$				1				$n-3$
$2^{n-3}-1$		1				-1				-1
$2^{n-2}-1$		1			-1	-7			-1	-7
$2^{n-1}-2^k-1$	$k=1\cdots n-3$	$n-3$				-1				$-n+3$
$2^{n-1}-1$		1		-1	-3	-8		-1	-3	-8
							1	$n-2$	$3n-7$	$\frac{1}{2}n^2+\frac{1}{2}n-30$

From the point of view of the matrix theory all that is necessary is to show that for sufficiently high temperatures the maximum characteristic value of $\mathfrak{M}(K)$ is no longer degenerate.

For high temperatures $K(=\frac{1}{2}J/kT)$ tends to zero and both α and β tend to unity. Thus for very high temperatures the matrices $\mathbf{V}_+(K)$ and $\mathbf{V}_-(K)$ are practically

$$\mathbf{V}_+(0)=\begin{Vmatrix} 1 & & & & & & 1 \\ & 1 & & & & 1 & \\ & & \ddots & & \iddots & & \\ & & & 1 & 1 & & \\ & & \iddots & & \ddots & & \\ & 1 & & & & 1 & \\ 1 & & & & & & 1 \end{Vmatrix},$$

$$\mathbf{V}_-(0)=\begin{Vmatrix} 1 & 1 & & & & & \\ & & 1 & 1 & & & \\ & & & & \ddots & & \\ & & & & & 1 & 1 \\ & & & & \iddots & -1 & -1 \\ & & -1 & -1 & & & \\ -1 & -1 & & & & & \end{Vmatrix}. \tag{6.1}$$

Taking a finite problem for which the matrices are of the order 2^r, one finds upon successive multiplication that the rth powers of $\mathbf{V}_+(0)$ and $\mathbf{V}_-(0)$ have the forms

$$\mathbf{V}_+(0)^r=\begin{Vmatrix} 1 & \cdots & 1 \\ 1 & \cdots & 1 \\ 1 & \cdots & 1 \\ \cdot & \cdots & \cdot \\ \cdot & \cdots & \cdot \\ 1 & \cdots & 1 \\ 1 & \cdots & 1 \end{Vmatrix},$$

$$\mathbf{V}_-(0)^r=\begin{Vmatrix} 1 & 1 & 1 & \cdots & 1 & 1 & 1 \\ -1 & -1 & -1 & \cdots & -1 & -1 & -1 \\ 1 & 1 & 1 & \cdots & 1 & 1 & 1 \\ \cdot & \cdot & \cdot & \cdots & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdots & \cdot & \cdot & \cdot \\ -1 & -1 & -1 & \cdots & -1 & -1 & -1 \\ 1 & 1 & 1 & \cdots & 1 & 1 & 1 \end{Vmatrix}. \tag{6.2}$$

$\mathbf{V}_+(0)^r$ consists entirely of ones while $\mathbf{V}_-(0)^r$ has alternate rows of ones and minus ones. Since the matrices are of rank one, their characteristic equations reduce to the form

$$\lambda^{2^r}-(\text{trace } \mathbf{V}_\pm(0)^r)\cdot\lambda^{2^r-1}=0. \tag{6.3}$$

The trace of $\mathbf{V}_+(0)^r$ is 2^r. Therefore the characteristic values of $\mathbf{V}_+(0)^r$ are 2^r, 0, 0, $\cdots$, 0 and hence the maximum characteristic value of $\mathbf{V}_+(0)$ is 2 and all the rest are 0. The trace of $\mathbf{V}_-(0)^r$ vanishes, however. As a result all of its characteristic values and hence all the characteristic values of $\mathbf{V}_-(0)$ vanish.

This proves that for sufficiently high temperatures the maximum characteristic value of $\mathfrak{M}$ is non-degenerate and that there is therefore no long range order.

7. The Propagation of Order

The principal advantage that can be claimed for the matrix method is that it provides a solution not only to the problem of the long range order, but also to the more general problem of the propagation of order throughout the lattice. For example, suppose that a certain site in the crystal is known to be occupied by a + atom. We can then investigate how this knowledge affects the probability for + (or −) atoms at *all* other sites and see the gradual transition from the strong short range influence of the fixed + atom to the weaker long range influence which is described by the long range order. This is the problem originally proposed by Zernike. Moreover, using the matrix method we can investigate the propagation of order for more complicated initial configurations consisting of several atoms. Thus we shall find the ordering effect of a pair of fixed atoms, of combinations of three, four atoms, and so on, in each case observing the change from the short to the long range effect.

Zernike's Problem. The Transition from Short to Long Range Order

If the expression (5.1) for $P(\alpha_1, \alpha_r)$ is summed over all configurations α_r, one finds for the probability of a configuration α_1, in pitch number 1

$$P(\alpha_1)=\frac{1}{\sum_p \lambda_p{}^{mn}}\sum_p \lambda_p{}^{mn}\mathbf{B}_p(\alpha_1)\mathbf{A}_p(\alpha_1).$$

At low temperatures and for ferromagnetic crystals, the twofold degeneracy of $\lambda_{\max}$ leads to the expression (dropping the subscript 1)

$$P(\alpha)=\tfrac{1}{2}(\mathbf{B}_+(\alpha)\mathbf{A}_+(\alpha)+\mathbf{B}_-(\alpha)\mathbf{A}_-(\alpha))$$
$$=\mathbf{B}_+(\alpha)\mathbf{A}_+(\alpha). \quad (7.1)$$

This is in marked analogy with the quantum mechanics, where the probability density is proportional to the wave function multiplied by its complex conjugate. From (7.1) we can also see that the theory is entirely symmetrical in the two kinds of atoms, + and −. Thus if we make a transformation which takes a configuration α into one $\bar{\alpha}$ obtained from it by changing all + atoms to − atoms, and conversely, we find from (3.10) and (3.11) that $\mathbf{B}_+(\alpha)=\mathbf{B}_+(\bar{\alpha})$ and $\mathbf{A}_+(\alpha)=\mathbf{A}_+(\bar{\alpha})$, so that $P(\alpha)=P(\bar{\alpha})$. This symmetry is evidently necessary, since + and − atoms have been treated equally from the start, the energy of interaction between a pair of + atoms being equal to the energy of interaction of a pair of − atoms.

Any question concerning the probability of a certain disposition of atoms on lattice sites all in one pitch is answered by summing $P(\alpha)$ over all configuration α consistent with the restrictions proposed. We shall, therefore, always have to deal with the expressions of the type

$$\sum_\alpha{}' \mathbf{B}_+(\alpha)\mathbf{A}_+(\alpha)=\frac{\sum_\alpha{}' \boldsymbol{\phi}_+(\alpha)\boldsymbol{\psi}_+(\alpha)}{2\bar{\boldsymbol{\phi}}_+\boldsymbol{\psi}_+}=\frac{\bar{\boldsymbol{\phi}}_+\boldsymbol{\psi}_+-\mathbf{V}}{2\bar{\boldsymbol{\phi}}_+\boldsymbol{\psi}_+}, \quad (7.2)$$

where the prime indicates that the summation is to be taken over the configurations allowed by the restrictions, and V is the sum of $\boldsymbol{\phi}_+(\alpha)\boldsymbol{\psi}_+(\alpha)$ over the suppressed configurations. The sum V is generally easier to carry out than the direct sum over the allowed configurations.

Let us now apply (7.2) to the investigation of the ordering influence of one atom on its neighbors in the same line of the crystal. Let $P(+_1r_2)$, $P(+_1r_3)$, $\cdots$, $P(+_1r_p)$,[17] be the probability of finding a + atom at a site conveniently called 1 and then an atom rightly ordered with respect to it at a distance of one site away, two sites away, . . . , $(p-1)$ sites away, respectively. We can write $P(+_1r_p)$ as equal to the probability for finding a + atom at the site 1 in the lattice multiplied by the probability that the right atom is found $p-1$ sites away when it is already known that a + atom exists at site 1. The latter correlation probability we denote by $C(+_1|r_p)$ and take it as a measure of the ordering influence of a single + atom. Of course

$$P(+_1r_p)=\tfrac{1}{2}C(+_1|r_p).$$

[17] This r notation is used so as not to distinguish between the ferromagnetic and antiferromagnetic cases. The calculations will be made for the ferromagnetic case, but it will be shown that the results are valid in the other as well. For the ferromagnetic case, r_2, for example, would be $+_2$ while for the antiferromagnetic case it would be $-_2$.

These correlation probabilities are easily calculated from a table of values of $\phi_+(\alpha)\psi_+(\alpha)$ similar to that given in Table II. For example, if, in (7.2), we make the restriction that the last two atoms, numbers $n-1$ and $n-2$ are both $+$ we have the conditions necessary for the calculation of $C(+_1|r_2)$. Similarly, for $C(+_1|r_3)$ we would hold the atoms $n-1$ and $n-3$ fixed as $+$. We find

$$\begin{aligned}
C(+_1|r_2) &= 1-2\beta^4-6\beta^6-18\beta^8 \\
&\quad -60\beta^{10}-224\beta^{12}-\cdots, \\
C(+_1|r_3) &= 1-2\beta^4-8\beta^6-30\beta^8 \\
&\quad -112\beta^{10}-430\beta^{12}-\cdots, \\
C(+_1|r_4) &= 1-2\beta^4-8\beta^6-32\beta^8 \\
&\quad -134\beta^{10}-576\beta^{12}-\cdots, \\
C(+_1|r_5) &= 1-2\beta^4-8\beta^6-32\beta^8 \\
&\quad -136\beta^{10}-612\beta^{12}-\cdots, \\
C(+_1|r_6) &= 1-2\beta^4-8\beta^6-32\beta^8 \\
&\quad -136\beta^{10}-614\beta^{12}-\cdots, \\
C(+_1|r_7) &= 1-2\beta^4-8\beta^6-32\beta^8 \\
&\quad -136\beta^{10}-614\beta^{12}-\cdots,
\end{aligned} \tag{7.4}$$

and $C(+_1|r_p)=C(+_1|r_6)$ to terms of order β^{12} for $p\geqq 7$.

The correlation probability, $C(+_1|r_p)$, has its maximum value of unity at the absolute zero of temperature ($\beta=0$) and for finite temperatures ($\beta>0$) falls off monotonically as one goes further from the central site at which the $+$ atom is situated. Examining the sequence (7.4) we find that the coefficients of the various powers of β increase monotonically in absolute value until they reach a certain limit, the approach to the limit being rapid at first and then slower at the end. For the lower powers of β this approach to the limiting value occurs earlier in the sequence than it does for the higher powers. Thus, from (7.4),

$$\begin{aligned}
C(+_1|r_2) > C(+_1|r_3) > C(+_1|r_4) \\
> C(+_1|r_5) > C(+_1|r_6) > \cdots.
\end{aligned} \tag{7.5}$$

For $p\geqq 6$ we see that to terms of the order β^{12}, $C(+_1|r_p)$ becomes identical with the long range correlation (5.11). Denoting the long range correlation by $C(+_1|r_\infty)$ we have

$$C(+_1|r_\infty)=\tfrac{1}{2}(1+S^2). \tag{7.6}$$

In this approximation the long range effect is already attained five sites away from the central atom. This holds of course only for those temperatures for which terms of order higher than β^{12} can be neglected. As the temperature increases the transition to the long range limit takes place only after one goes considerably further from the central site.

The correlation probability $C(+_1|r_2)$ is closely related to the average energy of the crystal. Thus if Q_r stands for the probable number of right pairs of atoms each having an energy of interaction $-\frac{1}{2}J$ and Q_w for the number of wrong pairs of atoms each having an energy of $\frac{1}{2}J$, we have for the average energy

$$E=-\tfrac{1}{2}JQ_r+\tfrac{1}{2}JQ_w.$$

Remembering that for a crystal containing N atoms there are $2N$ pairs of nearest neighbors, we find

$$Q_r=2NC(+_1|r_2), \quad Q_w=2N\{1-C(+_1|r_2)\}$$

and

$$\begin{aligned}
E &= NJ\{1-2C(+_1|r_2)\} \\
&= -NJ+NJ(4\beta^4+12\beta^6+36\beta^8 \\
&\qquad +120\beta^{10}+448\beta^{12}+\cdots).
\end{aligned} \tag{7.7}$$

This series for E has been given before in (4.11) and was obtained there from the expansion of the maximum characteristic value λ_+. The present method is based on the characteristic vectors and the agreement between the two provides a check on the internal consistency of the results.

It is not necessary to confine oneself entirely to atoms on the same line with the fixed $+$ atom. For in virtue of the screwlike construction of the lattice, the atom at the end of the pitch, $n-1$, is situated near the atoms 0, 1, 2, $\cdots$ at the beginning of the pitch, as shown in Fig. 2. We can find the influence of a fixed $+$ atom at sites on the next line by applying (7.2) with the restrictions that atoms $n-1$ and 0, $n-1$ and 1, $n-1$ and 2, etc. are to be successively held fixed as $+$ atoms. The notation $C(^{+_1}|r_p)$ suggests

FIG. 2. The n sites of a single pitch.

itself for the correlation probabilities. The results are

$$\begin{aligned}
C(+_1|r_2) &= 1-2\beta^4-8\beta^6-26\beta^8 \\
&\quad -88\beta^{10}-326\beta^{12}-\cdots, \\
C(+_1|r_3) &= 1-2\beta^4-8\beta^6-32\beta^8 \\
&\quad -124\beta^{10}-484\beta^{12}-\cdots, \\
C(+_1|r_4) &= 1-2\beta^4-8\beta^6-32\beta^8 \\
&\quad -136\beta^{10}-594\beta^{12}-\cdots, \\
C(+_1|r_5) &= 1-2\beta^4-8\beta^6-32\beta^8 \\
&\quad -136\beta^{10}-614\beta^{12}-\cdots, \\
C(+_1|r_6) &= 1-2\beta^4-8\beta^6-32\beta^8 \\
&\quad -136\beta^{10}-614\beta^{12}-\cdots.
\end{aligned} \tag{7.8}$$

This sequence has the same properties as the sequence (7.4). A comparison of the two shows that

$$\begin{aligned}
&C(+_1|r_2)>C(+_1|r_2)>C(+_1|r_3) \\
&\quad >C(+_1|r_3)>C(+_1|r_4)>C(+_1|r_4)>\cdots
\end{aligned} \tag{7.9}$$

indicating again a monotonic decrease of the correlation probability as the distance from the fixed atom increases.

The correlation probabilities (7.4) and (7.8) do not constitute a complete solution of Zernike's problem since there are many distances between pairs of atoms which are not included. However, this is as far as one can go without a knowledge of the entire spectrum of characteristic values of the $\mathbf{V}_+$ matrix. This is because the expression for $P(\alpha_1, \alpha_r)$, where r is a small integer, cannot be simplified to the point where only the maximum characteristic value of $\mathbf{V}_+$ enters. Nevertheless the range of distances covered by (7.4) and (7.8) is fairly complete and for those that are left out, one can get good estimates of the coefficients of the smaller powers of β by applying the condition for monotonic decrease with distance.

It should be pointed out that the expressions found for the correlation probabilities are valid for antiferromagnetic crystals as well. As we see from (3.12), the vectors $\bar{\mathbf{B}}_\pm(-K)$, $\mathbf{A}_\pm(-K)$ applicable in this case have components which are identical except for the order with those of $\bar{\mathbf{B}}_\pm(K)$ and $\mathbf{A}_\pm(K)$ appropriate to the ferromagnetic case. The permutation matrix $\mathbf{R}$, carrying the one set of vectors into the other, carries each configuration into the one obtained from it by changing the sign of every alternate atom in it. Thus for $C(+_1|+_2)$, calculated in the ferromagnetic case, we summed over all the configurations for which atoms $n-1$ and $n-2$ were both $+$. The permutation matrix $\mathbf{R}$ carries these configurations into all those for which the atoms $n-1$ and $n-2$ are, respectively, $+$ and $-$. Therefore $C(+_1|+_2)$, as calculated in the ferromagnetic case, is equal to $C(+_1|-_2)$ for the antiferromagnetic case.

8. Comparison with the Results of Zernike

Carrying out Zernike's method for treating the propagation problem, we find in the case of two dimensions for the long range order and the correlation probabilities

$$\begin{aligned}
S &= 1-2\beta^4-8\beta^6-20\beta^8 \\
&\quad -48\beta^{10}-122\beta^{12}-\cdots, \\
C(+_1|r_2) &= 1-2\beta^4-6\beta^6-11\beta^8-\cdots, \\
C(+_1|r_2) &= 1-2\beta^4-8\beta^6-14\beta^8-\cdots, \\
C(+_1|r_3) &= 1-2\beta^4-8\beta^6-16\beta^8-\cdots, \\
C(+_1|r_4) &= 1-2\beta^4-8\beta^6-18\beta^8-\cdots, \\
C(+_1|r_p) &= C(+_1|r_4) \quad p\geqq 5 \quad \text{(to terms} \\
&\quad \text{of order } \beta^8).
\end{aligned} \tag{8.1}$$

Comparison with (5.10), (7.4), and (7.8) shows that Zernike's approximation at low temperatures is valid up to terms of the order β^6.

In three dimensions we make use of the series for S and $C(+_1|r_2)$ found by van der Waerden.[5] The comparison with Zernike is given in (8.2).

van der Waerden:

$$S=1-2\beta^6-12\beta^{10}+14\beta^{12}-90\beta^{14}+192\beta^{16}-792\beta^{18}+\cdots,$$

Zernike:

$$S=1-2\beta^6+6\beta^8+\cdots, \tag{8.2}$$

van der Waerden:

$$C(+_1|r_2)=1-2\beta^6-10\beta^{10}+14\beta^{12}-70\beta^{14}+176\beta^{16}-626\beta^{18}+\cdots,$$

Zernike:

$$C(+_1|r_2)=1-2\beta^6+6\beta^8+\cdots.$$

Zernike's method therefore seems to be better in two dimensions than it is in three. This can perhaps be understood from the following consideration. The essential approximation in Zernike's difference equation comes from the assumption that the probabilities for the atoms forming the nearest neighbors of a given atom, are independent of one another. Although no two of the atoms at these surrounding sites are nearest neighbors, the probabilities for them are not independent because of the possibility of interaction through intermediate atoms. The magnitude of the correlation will in some way be connected with the number of short paths of influence between the two atoms. In three dimensions, the correlation will presumably be greater because the number of available paths is certainly much greater than in two dimensions. We might therefore expect the approximation to get poorer as the dimension is increased. In one dimension, where the assumption of Zernike is least serious, it can be shown[18] that his solution is actually exact, although the method of deriving the equation involves an approximation.

9. The Ordering Influence of More Complicated Configurations

Next to a single + atom, the simplest initial arrangement to consider is an ordered pair of adjacent atoms, $+_1r_2$. Denoting by $P(+_1r_2r_j)$ the probability for finding a plus atom at a given site and two atoms rightly ordered with respect to it at sites adjacent and $(j-1)$ steps away, we have for the correlation probability

$$C(+_1r_2|r_j)=P(+_1r_2r_j)/P(+_1r_2).$$

Application of the methods of Section 7 gives

$$\begin{aligned}
C(+_1r_2|r_3)&=1-\beta^4-4\beta^6-17\beta^8-70\beta^{10}-291\beta^{12}-\cdots,\\
C(+_1r_2|r_4)&=1-\beta^4-5\beta^6-24\beta^8-109\beta^{10}-487\beta^{12}-\cdots,\\
C(+_1r_2|r_5)&=1-\beta^4-5\beta^6-25\beta^8-121\beta^{10}-580\beta^{12}-\cdots,\\
C(+_1r_2|r_6)&=1-\beta^4-5\beta^6-25\beta^8-122\beta^{10}-599\beta^{12}-\cdots,\\
C(+_1r_2|r_7)&=1-\beta^4-5\beta^6-25\beta^8-122\beta^{10}-600\beta^{12}-\cdots
\end{aligned} \tag{9.1}$$

and to terms of order β^{12}

$$C(+_1r_2|r_p)=C(+_1r_2|r_7), \quad p\geqq 8.$$

Comparison of (7.10) and (7.4) shows that in general

$$C(+_1r_2|r_j)>C(+_1|r_{j-1}).$$

Thus, as expected, an ordered pair of atoms is a more effective ordering influence than a single atom. The sequence (9.1) shows the same kind of approach to the long distance limit as do the sequences (7.4) and (7.8).

It will be interesting to compare the correlation probabilities for the ordered pair $+_1r_2$ with those for the ordered pair $^{+1}r_2$ where the atoms are separated by a distance $\sqrt{2}$ times the lattice distance. (See Fig. 3.) By imposing, in (7.2), the condition that the atoms $n-1$, 0, and $j-2$, of a single pitch be held fixed as + we find the probability $P(^{+1}r_2r_j)$. Dividing this by $P(^{+1}r_2)$ gives

FIG. 3. An ordered pair of atoms separated by a distance $\sqrt{2}$ (in units of the lattice distance).

[18] A. Nordsieck (unpublished).

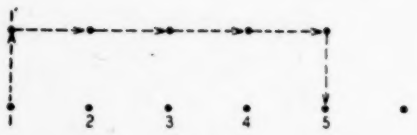

FIG. 4. The shortest path of influence from site 1 to site 5 when site 2 is occupied by a known atom.

the correlation probability $C(^{+1}r_2|r_j)$. The result is

$$\begin{aligned}
C(^{+1}r_2|r_3)&=1-\beta^4-3\beta^6-14\beta^8\\
&\qquad -62\beta^{10}-269\beta^{12}-\cdots,\\
C(^{+1}r_2|r_4)&=1-\beta^4-4\beta^6-20\beta^8\\
&\qquad -96\beta^{10}-447\beta^{12}-\cdots,\\
C(^{+1}r_2|r_5)&=1-\beta^4-4\beta^6-21\beta^8\\
&\qquad -107\beta^{10}-532\beta^{12}-\cdots,\\
C(^{+1}r_2|r_6)&=1-\beta^4-4\beta^6-21\beta^8\\
&\qquad -108\beta^{10}-550\beta^{12}-\cdots,\\
C(^{+1}r_2|r_7)&=1-\beta^4-4\beta^6-21\beta^8\\
&\qquad -108\beta^{10}-551\beta^{12}-\cdots
\end{aligned} \tag{9.2}$$

and to terms of order β^{12}

$$C(^{+1}r_2|r_p)=C(^{+1}r_2|r_7), \quad p\geqq 8.$$

The comparison of (9.1) with (9.2) shows that the pair $^{+1}r_2$ is a more effective ordering influence than the pair $+_1r_2$; that is

$$C(^{+1}r_2|r_j)>C(+_1r_2|r_j).$$

The reason for this can be easily understood. In the diagram of Fig. 4 let us consider the correlation probability at site 5, perhaps, for an ordered pair of atoms at sites 1 and 2 and then for an ordered pair at 1′ and 2. With the atom at 2 held fixed, the shortest path of influence from 1 to 5 consists of six steps and is shown by the dotted line. However, for the atom at site 1′, the shortest path of influence consists of only five steps. Thus, if site 2 is occupied by a known atom, placing a properly ordered atom at site 1′ will be more effective at 5 than placing an ordered atom at site 1. We should, therefore, expect $C(^{+1}r_2|r_5)$ to be larger than $C(+_1r_2|r_5)$.

If the correlation probabilities arising from an ordered pair of atoms are greater than the correlation probabilities arising from a single atom, we should find that the correlations for a disordered pair will be smaller than those for a single atom. We shall denote such a disordered pair, or "dipole," by $+_1w_2$. The correlation probabilities $C(+_1w_2|r_j)$ can be obtained from results already given. Thus, expressing the identity

$$P(+_1w_2r_j)+P(+_1r_2r_j)\equiv P(+_1r_j)$$

in terms of correlation probabilities, we have

$$C(+_1w_2|r_j)=\frac{C(+_1|r_j)-C(+_1|r_2)C(+_1r_2|r_j)}{1-C(+_1|r_2)}. \tag{9.3}$$

Here r_j means right with respect to the + atom at site 1.

From (7.4), (9.1), and (9.3) we have then

$$\begin{aligned}
C(+_1w_2|r_3)&=\tfrac{1}{2}(1-\beta^2-3\beta^4-8\beta^6-22\beta^8-\cdots),\\
C(+_1w_2|r_4)&=\tfrac{1}{2}(1\quad -\beta^4-8\beta^6-40\beta^8-\cdots),\\
C(+_1w_2|r_5)&=\tfrac{1}{2}(1\qquad -\beta^6-15\beta^8-\cdots),\\
C(+_1w_2|r_6)&=\tfrac{1}{2}(1\qquad\quad -\beta^8-\cdots),\\
C(+_1w_2|r_7)&=\tfrac{1}{2}(1\qquad\qquad -\cdots)
\end{aligned} \tag{9.4}$$

and to terms of order β^8

$$C(+_1w_2|r_p)=\tfrac{1}{2} \quad p\geqq 7.$$

These series show that at large distances the correlation probability arising from a dipole, $+_1w_2$, approaches the value $\frac{1}{2}$. The dipole therefore has no ordering influence at all at large distances, since the probability of finding a + or a − atom at a given lattice point when the dipole is not present is also equal to $\frac{1}{2}$. The atoms of the disordered pair thus have the tendency to annul each other's ordering effect, the cancellation being complete at infinite distance.

Many further examples of sequences of correlation probabilities could be given. Instead, however, we shall give in Table III a list of correlation probabilities for a line of the lattice from which all other correlations can be obtained by suitable combination. The table gives the correlation probabilities as a function of position in a line of the lattice for a sequence of initial configurations beginning first with one fixed +

atom, then an ordered pair of atoms, then 3, 4, 5, 6, etc. . . . consecutive ordered atoms.

For each fixed initial configuration, the correlation probability decreases monotonically with distance and tends to a limiting function at very large distance. This is the behavior exhibited by the sequences (7.4), (7.8), (9.1), (9.2), and (9.4). However, there is also an approach to a limit for sequences like

$$C(+_1|r_2),\quad C(+_1r_2|r_3),\quad C(+_1r_2r_3|r_4),\quad \cdots,$$
$$C(+_1\cdots r_j|r_{j+1}),\quad \cdots.$$

These probabilities show the ordering influence at a site immediately adjacent to stretches of ordered atoms of different lengths. The correlation appears to increase as the length of the ordered stretch increases. For stretches of six or more atoms, however, the correlation probabilities are identical, to terms of the order β^{12}. We can conclude, then, that to this order of accuracy the correlation probability at a point immediately adjacent to a completely ordered half-line, $r_{-\infty}\cdots r_{-2}r_{-1}+_0$ is given by

$$C(r_{-\infty}\cdots r_{-2}r_{-1}+_0|r_1)=1-\beta^4-3\beta^6-10\beta^8 -37\beta^{10}-149\beta^{12}-\cdots. \quad (9.5)$$

In the same way, the correlation probabilities for sites 2, 3, 4, 5, $\cdots$ steps away from the ordered half-line are given by

$$\begin{aligned} C(r_{-\infty}\cdots r_{-1}+_0|r_2)&=1-\beta^4-4\beta^6-16\beta^8 -64\beta^{10}-264\beta^{12}-\cdots,\\ C(r_{-\infty}\cdots r_{-1}+_0|r_3)&=1-\beta^4-4\beta^6-17\beta^8 -75\beta^{10}-338\beta^{12}-\cdots,\\ C(r_{-\infty}\cdots r_{-1}+_0|r_4)&=1-\beta^4-4\beta^6-17\beta^8 -76\beta^{10}-356\beta^{12}-\cdots,\\ C(r_{-\infty}\cdots r_{-1}+_0|r_5)&=1-\beta^4-4\beta^6-17\beta^8 -76\beta^{10}-357\beta^{12}-\cdots. \end{aligned} \quad (9.6)$$

To terms of order β^{12}

$$C(r_{-\infty}\cdots r_{-1}+_0|r_p)=C(r_{-\infty}\cdots r_{-1}+_0|r_5)\quad p\geqq 6.$$

For the long range effect of the ordered half-line we therefore have the expression

$$C(r_{-\infty}\cdots r_{-1}+_0|r_\infty)=1-\beta^4-4\beta^6-17\beta^8 -76\beta^{10}-357\beta^{12}-\cdots. \quad (9.7)$$

TABLE III. Correlation probabilities for the atoms in one line of the lattice.

	β^0	β^4	β^6	β^8	β^{10}	β^{12}
$C(+_1\|r_2)$	1	−2	−6	−18	− 60	−224
$C(+_1\|r_3)$	1	−2	−8	−30	−112	−430
$C(+_1\|r_4)$	1	−2	−8	−32	−134	−576
$C(+_1\|r_5)$	1	−2	−8	−32	−136	−612
$C(+_1\|r_6)$	1	−2	−8	−32	−136	−614
$C(+_1\|r_7)$	1	−2	−8	−32	−136	−614
$C(+_1r_2\|r_3)$	1	−1	−4	−17	− 70	−291
$C(+_1r_2\|r_4)$	1	−1	−5	−24	−109	−487
$C(+_1r_2\|r_5)$	1	−1	−5	−25	−121	−580
$C(+_1r_2\|r_6)$	1	−1	−5	−25	−122	−599
$C(+_1r_2\|r_7)$	1	−1	−5	−25	−122	−600
$C(+_1r_2\|r_8)$	1	−1	−5	−25	−122	−600
$C(+_1r_2r_3\|r_4)$	1	−1	−3	−11	− 50	−241
$C(+_1r_2r_3\|r_5)$	1	−1	−4	−17	− 78	−376
$C(+_1r_2r_3\|r_6)$	1	−1	−4	−18	− 89	−451
$C(+_1r_2r_3\|r_7)$	1	−1	−4	−18	− 90	−469
$C(+_1r_2r_3\|r_8)$	1	−1	−4	−18	− 90	−470
$C(+_1r_2r_3\|r_9)$	1	−1	−4	−18	− 90	−470
$C(+_1\cdots r_4\|r_5)$	1	−1	−3	−10	− 38	−170
$C(+_1\cdots r_4\|r_6)$	1	−1	−4	−16	− 65	−286
$C(+_1\cdots r_4\|r_7)$	1	−1	−4	−17	− 76	−360
$C(+_1\cdots r_4\|r_8)$	1	−1	−4	−17	− 77	−378
$C(+_1\cdots r_4\|r_9)$	1	−1	−4	−17	− 77	−379
$C(+_1\cdots r_4\|r_{10})$	1	−1	−4	−17	− 77	−379
$C(+_1\cdots r_5\|r_6)$	1	−1	−3	−10	− 37	−150
$C(+_1\cdots r_5\|r_7)$	1	−1	−4	−16	− 64	−265
$C(+_1\cdots r_5\|r_8)$	1	−1	−4	−17	− 75	−339
$C(+_1\cdots r_5\|r_9)$	1	−1	−4	−17	− 76	−357
$C(+_1\cdots r_5\|r_{10})$	1	−1	−4	−17	− 76	−358
$C(+_1\cdots r_5\|r_{11})$	1	−1	−4	−17	− 76	−358
$C(+_1\cdots r_6\|r_7)$	1	−1	−3	−10	− 37	−149
$C(+_1\cdots r_6\|r_8)$	1	−1	−4	−16	− 64	−264
$C(+_1\cdots r_6\|r_9)$	1	−1	−4	−17	− 75	−338
$C(+_1\cdots r_6\|r_{10})$	1	−1	−4	−17	− 76	−356
$C(+_1\cdots r_6\|r_{11})$	1	−1	−4	−17	− 76	−357
$C(+_1\cdots r_6\|r_{12})$	1	−1	−4	−17	− 76	−357
$C(+_1\cdots r_7\|r_8)$	1	−1	−3	−10	− 37	−149
$C(+_1\cdots r_7\|r_9)$	1	−1	−4	−16	− 64	−264
$C(+_1\cdots r_7\|r_{10})$	1	−1	−4	−17	− 75	−338
$C(+_1\cdots r_7\|r_{11})$	1	−1	−4	−17	− 76	−356
$C(+_1\cdots r_7\|r_{12})$	1	−1	−4	−17	− 76	−357
$C(+_1\cdots r_7\|r_{13})$	1	−1	−4	−17	− 76	−357

Comparing (9.7) and (5.10) we obtain the interesting result that

$$C(r_{-\infty}\cdots r_{-1}+_0|r_\infty)=\tfrac{1}{2}(1+S). \qquad (9.8)$$

The explanation of this identity would seem to be that the constraint of keeping an entire half-line ordered provides sufficient knowledge to decide which sites in the lattice are α sites and which are β sites, in the sense of Section 5. The probability for finding a right atom would then be given in terms of the long range order by (9.8) or (5.6).

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Statistics of Two-Dimensional Lattices with Four Components†

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We have considered a two-dimensional square net consisting of four kinds of atoms supposing that only nearest neighbors interact and that there are only two distinct potential energies of interaction, one between like and one between unlike atoms. In extension of a method due to Onsager it is found that for the case where like atoms attract one another a simple "reciprocity" relation exists between the partition functions at pairs of temperatures "reciprocally" related to one another. As one temperature T tends to zero, the other T^* tends to infinity. If one further assumes that only one "Curie" transition point exists, the relation between T and T^* enables one to locate the Curie temperature. Predictions can be made concerning the nature of the transition point with results similar to those of Kramers and Wannier. The reciprocity relation for the case of attraction between like atoms is found to be not valid for the case where unlike atoms attract one another.

INTRODUCTION

IN a recent paper[1] on the statistics of two-dimensional ferromagnets, Kramers and Wannier have given a treatment of a model for cooperative phenomena. They discovered an important property of their system which expressed itself in the form of a simple symmetrical relation between the partition functions Z and Z^* at pairs of temperatures T and T^*, related in a certain symmetrical way. Any knowledge of the partition function Z at temperature T implies an equivalent amount of knowledge about Z^* at the related temperature T^*. The relation between T and T^* is a one to one relation; T decreases monotonically if T^* increases so that $T\to 0$ as $T^*\to\infty$. There is only one temperature at which $T=T^*$. Assuming long range order at $T=0$ and absence of long range order at $T=\infty$, one will expect a Curie point. If the Curie point is the only temperature at which Z becomes singular, this temperature must be the one at which T and T^* become equal. Furthermore, one finds that the types of singularities which might occur at this transition are restricted by the relation between Z and Z^*. For example, if one assumes that there is no latent heat at the Curie point, the specific heat must be either continuous through the transition or infinite on both sides of the transition temperature.

Onsager[2] has been able to obtain the reciprocity relation discussed above from a more direct consideration of the form of the partition function. Moreover, his ingenious methods appear to lend themselves readily to generalization. Onsager proceeds by giving two formally different expressions for the partition function at a tempera-

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[1] H. A. Kramers and G. H. Wannier, Phys. Rev. 60, 252 (1941).

[2] This method has not yet appeared in print. We are greatly indebted to Dr. Onsager for his permission to make use of it.

ture T and at a temperature T^*. He is then able to produce a transformation between T and T^* which brings the first form of $Z(T)$ into a simple relation with the second form of $Z(T^*)$.

In this paper, Onsager's methods have been extended to the study of two-dimensional square lattices containing four kinds of atoms in equal abundance. In addition to the assumption that only the interaction of nearest neighbors are important, the further assumption is made that there are only two distinct energies of interaction, one between like and the other between unlike atoms. It must not be supposed that this restriction reduces the problem to that of a crystal with only two kinds of atoms, for in the four-component lattice the *a priori* probability of finding a given kind of atom at a lattice point is $\frac{1}{4}$ and not $\frac{1}{2}$.

The detailed investigation will show that for the case where like atoms attract one another a simple symmetry or "reciprocity" relation, in the sense of Kramers and Wannier, exists. The relation does not exist, however, if like atoms repel each other. One can understand this result by using the following qualitative consideration. At low temperatures, for the case where like atoms attract one another, minimum energy is attained when the atoms separate into regions consisting exclusively of like atoms; at high temperatures the atoms should be randomly distributed on the lattice sites. One might, therefore, expect a transition point where the long range order disappears. The situation is different when unlike atoms attract one another. Using the letters A, B, C, D to denote the four kinds of atoms, if, as is assumed, the unlike pairs, A–B, A–C, A–D, etc., attract and have the same energy of interaction, there are many different states of minimum energy, and from the presence of an A atom on a given site, one can draw no conclusion about the occupant of a distant site. Therefore, there is no long range order at low temperatures and no reason to expect an order-disorder transition.

1. FIRST FORM OF THE PARTITION FUNCTION

Consider a two-dimensional square lattice consisting of four kinds of atoms A, B, C, D. Suppose that only nearest neighbors interact and that the energies of interaction between the various pairs of nearest neighbors are given by the following scheme:

Pairs	A–A B–B C–C D–D	A–B	A–C	A–D
		C–D	B–D	B–C
Energy	ϵ	ϵ'	ϵ''	ϵ'''

The reason for splitting the six pairs of unlike atoms into three groups of two equivalent pairs each will appear later. Eventually, ϵ', ϵ'', ϵ''' will be taken as equal.

The first form of the partition function is given in terms of four auxiliary functions of the temperatures u, x, y, and z defined by the relations

$$\begin{aligned} \exp(-\epsilon/kT) &= u+x+y+z, \\ \exp(-\epsilon'/kT) &= u-x+y-z, \\ \exp(-\epsilon''/kT) &= u-x-y+z, \\ \exp(-\epsilon'''/kT) &= u+x-y-z. \end{aligned} \tag{1}$$

By a "configuration", denoted by the general letter c, we shall mean any particular distribution of the A, B, C, and D atoms on the various available lattice sites. The partition function Z, by using the grand canonical ensemble, is defined by

$$Z=\sum_c \exp(-E_c/kT),$$

where E_c is the total energy associated with the configuration c, and the summation is taken over all possible configurations. Since E_c is a certain linear combination of ϵ, ϵ', ϵ'', ϵ''', with integral coefficients, Z can also be written as

$$Z=\sum_c \left\{ \prod^c \exp\left(-\frac{\epsilon}{kT}\right) \prod^c \exp\left(-\frac{\epsilon'}{kT}\right) \times \prod^c \exp\left(-\frac{\epsilon''}{kT}\right) \prod^c \exp\left(-\frac{\epsilon'''}{kT}\right) \right\}, \tag{2}$$

where the numbers of factors in the various products depend, of course, on the configuration c. Since each pair of adjacent lattice sites contributes a factor to one of the four products in (2), we have, recalling the definitions of u, x, y, and z,

$$Z=\sum_c \Big\{ \prod_{\text{all pairs}}^c (u \pm x \pm y \pm z) \Big\}, \tag{3}$$

ATOM V	A	B	C	D
FACTOR	(+)(+)	(−)(+)	(−)(−)	(+)(−)

FIG. 1. An ineffective combination of lines.

where the product for each configuration is taken over all pairs of adjacent sites. This product can be evaluated by the following procedure: (i) for each pair of adjacent lattice sites, we choose a number which is either u, x, y, or z; (ii) examining the pairs of atoms assigned by the configuration c to the pairs of adjacent sites we attach the proper $+$ or $-$ signs to the x, y, or z factors chosen in (i) and multiply together the u, $\pm x$, $\pm y$, $\pm z$ factors for this choice; (iii) we repeat the procedure of (ii) for all possible choices made in (i) and add the results together, the sum giving the required product in (3) for the given configuration c.

The choice indicated in (i) can be specified in a more geometrical way if we draw in the lattice connecting lines labeled with an x, y, or z between all pairs of adjacent lattice sites for which an x, y, or z is selected. No connecting line is drawn between a pair for which the letter u is chosen in (i). In this way the choice in (i) is equivalent to a "pattern" of x, y, and z lines running through the lattice. Any configuration c of atoms in the lattice may be adopted for any pattern of lines p. For a given pattern p, the choice of signs in (ii) is determined by the configuration c. Therefore, the partition function may be written in the form of a double sum, summations being carried out over all configurations c, and over all patterns p.

$$Z=\sum_{c}\sum_{\text{patterns}}\{\prod^{p}u\prod^{p}\pm x\prod^{p}\pm y\prod^{p}\pm z\}. \quad (4)$$

The number of factors in each of the four products depends on the pattern p alone. The only effect of the configuration c is to influence the distribution of $+$ and $-$ signs.

There are many patterns, however, which do not effectively contribute to Z. In investigating the combinations of x, y, and z lines of a pattern which can intersect at a lattice point, we find that, under certain circumstances, there is a mutual cancellation of the four contributions to Z arising from a given pattern and four configurations which differ among themselves only in the identity of the atom at the lattice intersection point in question. For example, suppose that at a point a single x line and a single y line terminate. For any configuration, the contribution to Z of a pattern containing this combination of x and y lines intersecting, will evidently have a factor $(\pm x)\ (\pm y)$ arising from these intersecting lines. Let us consider this factor for each of the four configurations obtained from some arbitrary initial one by successively changing the identity of the atom V at the point of intersection, keeping the identities of all other atoms fixed. Looking at the definition of u, x, y, z for the signs, we have (Fig. 1) an ineffective combination of lines. The sum of these contributions vanishes. The same result is found for other initial configurations which place other atoms at the points 1 and 2. We conclude, therefore, that any pattern which contains the combination $x\,y$ at a point, does not effectively contribute to Z.

A different result (Fig. 2) is obtained for the combination of intersecting lines $x\,y\,z$. All these factors are of the same sign; their total contribution does not vanish. The same conclusion is reached for other atoms at points 1, 2, and 3.

Examining in this manner all the various combinations of lines which can intersect at a point, we find that for those patterns which are effective for Z, "effective patterns" for short, the combinations of intersecting lines must be among the following types:

$x\,x$	$x\,y\,z$	$x\,x\,x\,x$	$x\,x\,y\,y$
$y\,y$		$y\,y\,y\,y$	$x\,x\,z\,z$
$z\,z$		$z\,z\,z\,z$	$y\,y\,z\,z.$

Figure 3 gives an example of a typical effective pattern.

The effective combinations listed above have the property that the signs of their contributions to Z remain unchanged however one changes the identity of the atom at the point of intersection. From this we can prove that the contributions to Z of a given effective pattern p, are positive for all configurations of atoms c, and therefore are all equal and independent of c. This is evident if we

ATOM V	A	B	C	D
FACTOR	(+)(+)(+)	(−)(+)(+)	(−)(−)(+)	(+)(−)(+)

FIG. 2. An effective combination of lines.

consider that the contribution for a configuration of A atoms on all lattice points is surely positive, and that successive changes in the identities of the atoms at separate lattice points preserve the sign.

If N is the number of lattice sites, the total number of configurations is 4^N. Confining the summation to effective patterns and using the result of the previous paragraph, we can write as the final expression for the first form of the partition function

$$Z=4^N \sum_{\text{eff. patt.}} u^{2N-(l+m+n)} x^l y^m z^n, \qquad (5)$$

where l, m, n, are the total lengths (in units of the lattice distance) of the x, y, z lines, respectively, in one of the effective patterns contributing to the sum. Since there are $2N$ pairs of nearest neighbors when N is a large number and the factor u is chosen for all pairs of adjacent sites not included in the pattern, u appears to the power $2N-(l+m+n)$.

2. SECOND FORM OF THE PARTITION FUNCTION

The second form of the partition function is obtained by a geometrical procedure different from the one just used. For a given configuration, let us pick out all pairs of unlike nearest neighbors. Then, for each such pair, let us draw a separating line midway between the two atoms, this separating line being perpendicular to the line joining the pair and of length equal to the lattice distance. These separating lines will, from their definition, form the boundaries between regions in the lattice consisting of A atoms alone, B atoms alone, etc.

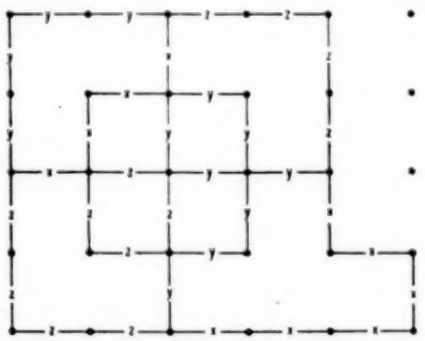

FIG. 3. A typical effective pattern.

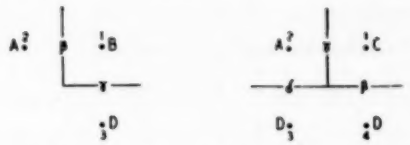

FIG. 4 (left). An impossible combination of lines.
FIG. 5 (right). A possible combination of lines.

Let us define four functions of the temperature $\alpha, \beta, \gamma, \delta$ by

$$\alpha=\exp\left(-\frac{\epsilon}{kT}\right), \quad \beta=\exp\left(-\frac{\epsilon'}{kT}\right),$$

$$\gamma=\exp\left(-\frac{\epsilon''}{kT}\right), \quad \delta=\exp\left(-\frac{\epsilon'''}{kT}\right) \qquad (6)$$

and proceed to label the boundary lines according to the following scheme in accordance with the fact that the energy between an A–B or C–D pair is ϵ' and so on.

Pairs of unlike atoms	A–B C–D	A–C B–D	A–D B–C
Label of separating line	β	γ	δ.

In this way, each configuration has associated with it a pattern of β, γ, δ lines. These patterns are not entirely arbitrary, however. For example, we cannot have a single β line and a single γ line terminating at a point. In Fig. 4, a B atom was assumed at 1, and the atoms 2 and 3 written down in accordance with our labeling scheme. The result is a contradiction, since the atoms at 2 and 3 are not separated by any line and must therefore have the same identity.[3] On the other hand, the combination $\beta\,\gamma\,\delta$ is possible, as Fig. 5 shows. If the identity of atom 1 is specified, the identities of atoms 2, 3, and 4 follow uniquely.

Examining all the cases, we find that the only possible combinations of β, γ, δ lines which can intersect at a point are among the following types:

$\beta\beta$	$\beta\gamma\delta$	$\beta\beta\beta\beta$	$\beta\beta\gamma\gamma$
$\gamma\gamma$		$\gamma\gamma\gamma\gamma$	$\beta\beta\delta\delta$
$\delta\delta$		$\delta\delta\delta\delta$	$\gamma\gamma\delta\delta$.

[3] The argument holds only for the interior of the two-dimensional crystal. The resulting reciprocity relation is proved, therefore, only for the case where surface effects may be neglected.

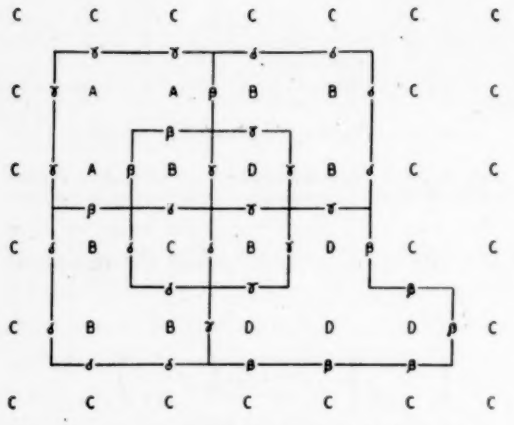

FIG. 6. β, γ, δ pattern identical with the x, y, z pattern of Fig. 3.

From this it can be concluded that, except for effects at the edges of the lattice which can be neglected when the lattice is very large, the patterns of β, γ, δ lines are geometrically identical with the effective patterns of x, y, z lines of the previous section. Figure 6 shows a pattern of β, γ, δ lines identical with the pattern of x, y, z lines of Fig. 3.

It is evident that each effective, or allowed, pattern of β, γ, δ lines is associated with exactly four distinct configurations. For if we give the identity of a particular atom in the lattice, the identities of all other atoms follow uniquely from the β, γ, δ pattern. The four configurations arise from the four possible identities of this particular atom. The energy of each of these configurations is

$$E_c=\{2N-(l+m+n)\}\epsilon+l\epsilon'+m\epsilon''+n\epsilon''', \quad (7)$$

where l, m, n are the respective lengths (in units of the lattice distance) of the β, γ, δ lines of the associated pattern. Remembering the factor four and the definitions of α, β, γ, δ, we can write the partition function as a sum over patterns, instead of configurations, giving

$$Z=4\sum_{\text{eff. patt.}}\alpha^{2N-(l+m+n)}\beta^l\gamma^m\delta^n. \quad (8)$$

The next step is to compare the expressions (5) and (8).

3. THE RECIPROCITY RELATION

We now introduce the assumption that all pairs of unlike nearest neighbors interact with the same energy; that is, we take $\epsilon'=\epsilon''=\epsilon'''$. As a consequence $x=y=z$ and $\beta=\gamma=\delta$. For convenience we shall write the energies ϵ and ϵ' in the form

$$\epsilon=-\omega+\phi$$
$$\epsilon'=\omega+\phi \quad (9)$$

and instead of the temperature, introduce as the new independent variable the quantity θ defined by

$$\theta=\exp(\omega/kT)=\alpha\exp(\phi/kT). \quad (10a)$$

We also define three new functions of the temperature U, X, η

$$U=u\exp(\phi/kT),$$
$$X=x\exp(\phi/kT), \quad (10b)$$
$$\eta=1/\theta=\beta\exp(\phi/kT).$$

Then from (1), (9), (10) and the equality of x, y, and z, it follows that

$$\exp[(\omega-\phi)/kT]=u+3x$$
$$=\exp(-\phi/kT)(U+3X),$$
$$\exp[(-\omega-\phi)/kT]=u-x \quad (11)$$
$$=\exp(-\phi/kT)(U-X).$$

The quantity ϕ can evidently be eliminated from these equations and one finds for U and X as functions of θ, the expressions

$$X=\tfrac{1}{4}[\theta-(1/\theta)],$$
$$U=\tfrac{1}{4}[\theta+(3/\theta)]. \quad (12)$$

Let us now consider the partition function at two temperatures T and T^* which are, so far, unrelated to one another, writing $Z=Z(T)$ in the form (5) and $Z^*=Z(T^*)$ in the form (8). For $l+m+n$ we shall write t. Using (10) to express u, x, α, β in terms of U, X, θ, η we have

$$Z=4^N\sum_{\text{eff. patt.}}u^{2N-t}x^t$$
$$=4^N\exp(-2N\phi/kT)U^{2N}\sum_{\text{eff. patt.}}(X/U)^t, \quad (13)$$

$$Z^*=4\sum_{\text{eff. patt.}}\alpha^{*2N-t}\beta^{*t}$$
$$=4\exp(-2N\phi/kT^*)\theta^{*2N}\sum_{\text{eff. patt.}}(\eta^*/\theta^*)^t$$
$$=4\exp(-2N\phi/kT^*)\theta^{*2N}\sum_{\text{eff. patt.}}(1/\theta^{*2})^t. \quad (14)$$

By a "reciprocity" relation between Z and Z^* we understand the following. There shall exist a transformation $T^*=F(T)$ between the temperatures T and T^* having the two properties (i) if T is carried into T^* by the transformation, the transformation also carries T^* into T; that is, if $T^*=F(T)$, then $T=F(T^*)$, (ii) for this transformation there shall exist a simple function $G(T)$ whose form is readily obtained without explicity evaluating the partition function and which is such that

$$G(T)Z(T)=G(T^*)Z(T^*). \tag{15}$$

Moreover, with the possible exception of the points $T=0$ and $T=\infty$, $G(T)$ shall have no singularities for real temperatures. If these conditions are satisfied one can conclude that if $Z(T)$ has a singularity at T, $Z(T^*)$ will have a corresponding singularity at T^*.

A comparison between (13) and (14) suggests that the transformation between T and T^* is the one given implicitly in the condition

$$\theta^{*2}=U/X. \tag{16}$$

We shall verify that (16) leads to a reciprocity relation in the sense previously described.

Writing U and X in terms of θ we see that (16) is equivalent to

$$\theta^{*2}=(\theta^2+3)/(\theta^2-1). \tag{17}$$

Solving for θ^2 gives

$$\theta^2=(\theta^{*2}+3)/(\theta^{*2}-1), \tag{18}$$

so that the transformation from T into T^* is of the required type.

Substituting (16) into (14) and comparing with the expression for Z in (13) we have

$$\tfrac{1}{4}\exp(2N\phi/kT^*)Z^*=(U/X)^N\sum(X/U)^i$$
$$=(4UX)^{-N}\exp(2N\phi/kT)Z. \tag{19}$$

The relation to be derived is most simply expressed in terms of the Nth root of Z, hereafter denoted by λ. This quantity may be regarded as the partition function per particle. In taking this Nth root, however, we shall replace $4^{1/N}$ by unity. To this extent, and to the extent that effects due to the edge of the crystal are neglected, our method of deriving the reciprocity relation is restricted to very large crystals. Writing $\lambda=Z^{1/N}$ and performing the Nth root we have

$$\exp(2\phi/kT^*)\lambda^*=(4UX)^{-1}\exp(2\phi/kT)\lambda. \tag{20}$$

Using (12), (17), and (20) one may verify the expression

$$\exp(2\phi/kT)\lambda=(4U^*X^*)^{-1}\exp(2\phi/kT^*)\lambda^* \tag{21}$$

obtained in a formal way from (20) by interchanging starred and unstarred quantities. From (20) and (21) the symmetrical relation

$$(U^*X^*)^{-\frac{1}{4}}\exp(2\phi/kT^*)\lambda^*$$
$$=(UX)^{-\frac{1}{4}}\exp(2\phi/kT)\lambda \tag{22}$$

readily follows. This has the form of a reciprocity relation.

If we define functions $f(\theta)$ and $\psi(\theta)$ by

$$f(\theta)=4\theta^{1+2\phi/\omega}/[(\theta^2+3)(\theta^2-1)]^{\frac{1}{4}},$$
$$\psi(\theta)=f(\theta)\lambda(\theta) \tag{23}$$

the reciprocity is also expressed by

$$\psi(\theta^*)=\psi(\theta). \tag{24}$$

The $f(\theta)$ defined here plays the role of $G(T)$ of (15). Since its only singularities are at $\theta=\infty$ and $\theta=1$ or $T=0$ and $T=\infty$, this requirement on $G(T)$ is also satisfied.

In the formal procedure outlined so far it has not been specified whether like or unlike atoms attract one another. For the case where like atoms attract one another, we have ϵ' greater than ϵ and hence $\omega>0$. The quantity θ is therefore greater than unity and from (17) θ^{*2} is positive and also greater than unity. Thus the transformation (17) is entirely consistent and the reciprocity relation (22) is valid.

However, for the case where like atoms repel one another, the energy ϵ' must be less than the energy ϵ, or ω must be negative. Consequently $\theta<1$. From (17), θ^{*2} would then be negative and would not correspond to any real temperature T^*. The conclusion is, therefore, that for repulsion between like atoms no reciprocity relation, in the sense defined above, is found.

It has been pointed out in the introduction that long range order at low temperatures exists if like atoms attract but not when they repel each other. Therefore, in these two cases, an essentially

different behavior of the partition function at low temperatures is to be expected while no such difference at high temperatures is anticipated. Thus it is reasonable to find that a correlation between behaviors at high and low temperatures found for the one case does not hold for the other.

It must not be supposed that no relation of the form (15) can exist for the case of repulsion between like atoms. In fact an infinite number of such relations is possible. As an example, suppose T and T^* are related by $TT^*=T_0^2$. Let $G(T)=Z(T_0^2/T)$. Then we can evidently write

$$G(T)Z(T)=G(T^*)Z(T^*).$$

But now no conclusion about $Z(T)$ can be drawn since the form of $G(T)$ remains unknown as long as that of $Z(T)$ is not known.

Returning to the case of attraction between like atoms we see that from (17) T^* is a monotonically decreasing function of T. As T increases from 0 to ∞, T^* decreases from ∞ to 0. There is only one temperature, which we shall denote by T_c, for which $T=T^*$. From (17) this occurs at

$$\theta_c=\exp(\omega/kT_c)=\sqrt{3}. \tag{25}$$

The interval from 0 to T_c is mapped by the transformation upon the interval from ∞ to T_c. Knowledge of λ on one of these intervals is equivalent, by (22), to knowledge of it on the other. If λ has any singularity at temperature T, it will have the same type of singularity at T^*. If it is assumed that only one singularity exists, it must then occur at temperature T_c, which we shall now call the critical temperature.

In Eq. (25) the quantity ω is half the difference between the energies of interaction between like and unlike atoms. The critical point for the two component system of Kramers and Wannier is given by

$$\theta_c^2=\exp(2\omega/kT_c)=1+\sqrt{2}, \tag{26}$$

where ω has the same significance as in our case. It will be noted that, for the same numerical value of ω, the transition occurs in our case at a temperature lower than the transition temperature of Kramers and Wannier by the ratio of $\ln(1+\sqrt{2})$ to $\ln 3$ or by a factor of about 0.8. This may be due to the fact that in the four-component system the *a priori* probability favors disorder more than in the two-component system so that long range order breaks down at a lower temperature. This consideration gives support to the view that θ_c corresponds to the "Curie point."

The existence of the reciprocity relation (22) or (24) enables us to make certain limited statements concerning the nature of the hypothetical transition point. These conclusions are identical with those of Kramers and Wannier for lattices with two components. The energy E and specific heat C are given in terms of λ by

$$E=-Nd\log\lambda/d(1/kT)=-N\omega\theta d\log\lambda/d\theta,$$

$$C=dE/dT=(-\omega\theta/kT^2)(dE/d\theta).$$

From (17) and (24) we find for the possible discontinuities in E and C at the critical point

$$\Delta E=-2N\omega\theta_c(d\log\psi/d\theta)_{\theta_c+0},$$

$$\Delta C=(\omega/kT_c^2)\Delta E. \tag{27}$$

Thus, if the energy is discontinuous, so is the specific heat. If $\Delta E=0$ the specific heat is either continuous or becomes infinite at the transition temperature in such a way that the difference in its values at T and T^* tends to zero as T tends to T_c. This is about as far as one can go with the reciprocity relation alone.

Letters to the Editor

PROMPT publication of brief reports of important discoveries in physics may be secured by addressing them to this department. The closing date for this department is the third of the month. Because of the late closing date for the section no proof can be shown to authors. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents. Communications should not in general exceed 600 words in length.

The Shape of Betatron Pole Faces

JAMES H. BARTLETT
Department of Physics, University of Illinois, Urbana, Illinois
August 25, 1943

FOR there to be focusing of the electron beam in the betatron, it is necessary that the magnetic field near the beam fulfill certain requirements.[1] In practice, these have been met by selecting a certain shape of pole face, determining the field by approximate methods such as flux plotting, and then modifying the original shape if it was not a suitable one. It is the purpose of this note to point out that the pole face shape may be determined in a more direct manner.

As in the article of Kerst and Serber, we use cylindrical coordinates, and $z=0$ describes the median plane. In empty space, curl $H=0$ and div $H=0$, so that $H=-\text{grad}\ \varphi_m$, where φ_m is the magnetostatic potential, and $\nabla^2\varphi_m=0$. We shall assume that $H_z(r)$ at $z=0$ is a known function, which is such that it satisfies the focusing conditions. A surface of constant magnetostatic potential will be, to a high degree of approximation, an acceptable boundary for the magnet. The problem thus reduces to the calculation of φ_m subject to the condition at $z=0$. In what follows, we drop the subscript m.

We require the solution of:

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial\varphi}{\partial r}\right)+\frac{\partial^2\varphi}{\partial z^2}=0.$$

Expand φ as a power series in z, so that:

$$\varphi=\sum_{n=0}^{\infty}\varphi_n(r)z^n. \tag{1}$$

Substituting in the differential equation, one obtains the recursion formula:

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial\varphi_n}{\partial r}\right)+(n+1)(n+2)\varphi_{n+2}=0. \tag{2}$$

Now:

$$H_z=-(\partial\varphi/\partial z)=-\Sigma n\ \varphi_n z^{n-1}.$$

Therefore, $(H_z)_{z=0}=-\varphi_1$. The potential φ_0 is arbitrary and may therefore be set equal to zero. The solution (1) of the problem is thus obtained by differentiating expressions involving φ_1 [as prescribed by (2)], and will be an odd function of z.

If the series (1) should prove to be valid in too narrow a range, one could extend the range by analytic continuation, i.e., a power series in $z-z_0$, where z_0 is such a value that φ may be readily calculated by (1).

[1] Stated by Kerst and Serber, Phys. Rev. 60, 58 (1941).

Proceedings of the American Physical Society

Meeting at Stanford University, July 10, 1943

THE 256th meeting of the American Physical Society was held at Stanford University, on Saturday, July 10, 1943. In spite of the "unusual" conditions prevailing on the campus, due to the presence of very large numbers of students in the armed forces, completely satisfactory arrangements for the meeting had been made, in accordance with the usual Stanford tradition. The average attendance at the two sessions was about 55, which nearly equals the average attendance at previous Stanford meetings. Some fifty members of the society and guests had luncheon together in the banquet room of Wilson's Restaurant, Palo Alto. Brief remarks were made at the luncheon by Professor Paul Kirkpatrick who, as chairman of the host department, also presided at the scientific sessions; by Dr. K. K. Darrow; and by the Local Secretary. The chief topic of these remarks was the trying situation in which all physics departments now find themselves, as the result of the specialized programs now being offered to large numbers of the armed forces.

Because of an expected dearth of contributed papers, arrangements had been made for three invited papers, and the success of the meeting was undoubtedly due in great measure to these papers. They were as follows:

Recent Developments in Electron Microscopy. L. Marton, *Division of Electron Optics, Stanford University.*

The Applications of Nuclear Physics to Medicine and Biology. Hardin Jones, *Radiation Laboratory, University of California.*

Entropy and Probability. K. K. Darrow, *Bell Telephone Laboratories.*

Dr. Hardin Jones, in connection with his paper, gave experimental demonstrations with an automatic recording Geiger counter, using a live mouse, on which he performed a surgical operation in full view of the audience.

There were twelve contributed papers, for which the abstracts are appended. None of these was read by title, which, I believe, constitutes a new record.

R. T. Birge
Local Secretary for the Pacific Coast

Abstracts of Contributed Papers

1. The Validity of Lens Equation and Magnification Formula of Light Optics for Electron Lenses. R. G. E. Hutter, *Division of Electron Optics, Stanford University.*—The usefulness of the lens equation $(Z_0-ZF_0)\cdot(Z_i-ZF_i) = -F_0\cdot F_i$ of the magnification formula $M=F_0/(Z_0-ZF_0)$ of light optics, and of the simple geometrical image construction based upon these equations, lies in the fact that the set of lens constants-focal points ZF_0, ZF_i, and focal lengths F_0, F_i are characteristics of the lens and are independent of the object position. It has often been shown that these equations also apply to electron optical lenses. These proofs assume, however, that the lens fields are of finite extent on the optical axis and that object and image are outside the lens region. The assumptions are of the nature of sufficient conditions only; i.e., electron lenses exist for which none of these conditions holds and yet the lenses can be characterized by a single set of optical constants. Necessary and sufficient conditions for such lens types are stated and an analytical expression for all lenses is derived. A number of simple magnetic and electrostatic lenses satisfying these conditions are discussed.

2. Optimum Conditions for Apertures of Magnetic Electron Lenses of the Field Form $H(Z)=H_0/(1+(Z/a)^2)$. L. Marton and R. G. E. Hutter, *Division of Electron Optics, Stanford University.*—It has been shown previously that the optical properties of strong magnetic lenses of the field form $H(Z)=H_0/(1+(Z/a)^2)$ can be completely calculated. Such calculations up to now did not include the position of the lens aperture. Furthermore, the size of the aperture was derived from considerations of the aberrations of weak lenses only. By using the complete analytical expression for the electron path through a lens, both location and size of such an aperture can be calculated. This aperture achieves the ray-limiting effect at a maximum value of its diameter. The calculated size and location of the aperture differs considerably from the values currently adopted. Diagrams are given for the aperture size and location in function of such parameters which allow their application to lenses of different strength and magnification.

3. Intensity of High Energy Electrons and Photons at 10,000 Feet. WAYNE E. HAZEN, *University of California.*— A cloud chamber containing eight 0.7-cm lead plates was operated without counter control at an altitude of 10,000 ft. High energy electrons and photons produced cascade showers in the lead plates whereas mesotrons produced only an occasional collision electron. Usually the shower maxima were observed, since the 30 by 30 cm chamber size provided a large solid angle and there was sufficient lead to produce maxima even in showers of several hundreds of particles. In 8500 photographs, 1090 showers that reached a maximum of four or more particles were observed. If we use the number of particles at the maximum as a measure of the energy of the incident particle, the differential energy spectrum for electrons plus photons of energy 2×10^8 to 10^9 ev follows an $E^{-2.4}$ distribution. When combined with Greisen's[1] counter data for electrons with energy greater than 2×10^7 ev, the present results indicate an $E^{-2.6}$ distribution. The intensity of electrons plus photons with energies greater than 2×10^8 ev relative to penetrating particles was found to be 8.5 percent.

[1] K. Greisen, Phys. Rev. 61, 212 (1942).

4. A Possible New Application of the Wilson Cloud Chamber. CARL E. NIELSEN, *University of California.*— It is well known that the atmosphere contains objects that serve as condensation nuclei with very small supersaturations. Such nuclei—which have interested physicists primarily in being objects that must be removed before the Wilson cloud chamber is useful for the study of ions—may, it is commonly supposed, be inert dust particles as well as salt particles and certain other chemicals. However, it has been asserted that condensation cannot occur upon "ordinary" dust particles. The experiments to be described have shown that dust (carbon) particles 0.5 micron in diameter, and also bacteria of dimensions 0.5 micron to 2 microns do serve as condensation nuclei with small supersaturations. Consequently it is possible to use the cloud chamber to precipitate bacteria from the air upon a petri dish containing agar culture medium. Unlike most common air sampling techniques, which give an unknown percent removal, this method removes *all* of the bacteria from the air.

5. Townsend Currents in Non-Uniform Electric Fields. PAUL L. MORTON, *University of California.* (*Introduced by Leonard B. Loeb.*)—The current in the Townsend discharge in nearly uniform fields and in the absence of secondary effects can be calculated from the equation $\log i/i_0=\int\alpha dx$, where the coefficient α as a function of the field intensity can be taken from the experimental work of Hale and others. Uniform fields seldom occur because of space charge distortion as well as electrode shape. The accuracy of this calculation has therefore been investigated for the field between concentric cylinders, in hydrogen at pressures from 0.01 to 10 millimeters, with currents sufficiently small to avoid space charge effects. The results indicate that large errors should be expected when the field intensity near the cathode changes by more than 10 percent per electron mean free path even when the gap is comparatively long, and that the calculated currents can be orders of magnitude off when the electrons reach the anode before attaining a terminal drift velocity corresponding to the field there. If the field changes rapidly only near the cathode and the gap is long, the total ionization as calculated may be approximately correct, even when its location, as indicated by the magnitude of α, is greatly in error. This fact accounts for the approximate agreement sometimes found when the Townsend equation is applied to glow discharges.

6. Apparent Failure of the Meek Criterion for Streamer Formation. LEON H. FISHER, *University of California.*— The criterion for streamer formation given by Meek is that the positive space charge field of an electron avalanche be equal to K times the impressed field. Measurements of streamer onset in confocal paraboloid gaps by Weissler and Loeb[1] indicate that K is extremely pressure dependent. In hydrogen and dry air, K decreases rapidly with decreasing pressure. The possibility existed that the method used in calculating the space charge field in a non-uniform gap was not valid. To test this, the cathode of the least uniform gap of Weissler and Loeb was illuminated with ultraviolet light, and measurements of the current below onset were made in hydrogen. The results indicate that the ionization in these divergent fields cannot be calculated by integrating the ionization functions for uniform fields. At a constant pressure, the current-voltage curve increases too rapidly with voltage. This effect becomes more pronounced with decreasing pressure. Morton has obtained similar results (paper No. 5) in much less divergent fields in hydrogen at pressures near one millimeter. The present results explain the observed trend in K, and restore the possibility of its physical significance. Measurements in air were also attempted, but no currents below streamer onset could be measured. This observation can be explained by electron attachment to oxygen molecules in the weak portion of the field.

[1] Weissler and Loeb, Phys. Rev. 62, 300 (1942).

7. The Effect of Adsorbed Gas on the Contact Electrification of Quartz on Nickel. DAVID E. DEBEAU, *University of California.*—The contact electrification of quartz particles in falling from one Ni container to a second Ni container has been measured as a function of gas pressure. When the gas used is air or O_2, the magnitude of the charge collected is a minimum at pressures of about 0.1 to 1.0 mm of Hg. The charge collected at 10^{-5} mm and at 760 mm is approximately the same. The maximum charge collected in one run is about 80 e.s.u. and the quartz and the Ni receiver become negative. When H_2 is used, no consistent results are obtainable and the charge collected is low. Not until the chamber is baked out in the presence of air are consistent results again obtainable with air or O_2 in the chamber.

8. Time Variation of Fog and Pressure in a Wilson Cloud Chamber. MORRIS NEUSTADT, *University of California.*— Fog and pressure were measured electrically, and were

observed as traces on an oscilloscope, an electron switch showing them simultaneously. The chamber was operated (1) saturated with water, (2) dry, (3) saturated with alcohol-water solution, 3 to 1 by volume. All measurements were made both for expansion to constant final volume, and to constant final pressure. Expansion ratios ranged from below the ion limit to above the fog limit. The larger the expansion ratio the larger is dp/dt after expansion. When large fog is present there is a rapid build-up of pressure due to heat of condensation of the fog. This effect on the pressure is not present when a dry chamber is used. If one expands below the ion limit, dense fog present from a previous over-expansion causes the pressure minimum to be higher, and causes the pressure to rise very sharply for a short time. As R increases, the fog builds up sooner and has a larger maximum value. Initially the fog increases as t^3, but during the sensitive time this relationship gradually changes, and the fog increases as t after the end of the sensitive time. Constant pressure fogs scatter more light than constant volume fogs.

9. Spectrographic Determination of Lead in Pectinous Materials. C. RULON JEPPESEN* AND E. JOHN EASTMOND, *Western Regional Research Laboratory.*—A spectrographic method of analysis for lead in pectinous materials has been developed which utilizes dry-ashed samples and thus avoids possible contamination from chemical treatments and the difficulties encountered in putting certain of these materials into solution. The dry-ashed sample is mixed with four times its weight of a standard buffer base consisting of 0.175 percent bismuth in lithium carbonate. A 250-volt d.c. arc between graphite electrodes is used as a source of excitation. The ratio of the intensities of the lines Pb 2833A and Bi 2898A is determined from photometric measurements of the spectrogram and the concentration of lead is read from a previously prepared working curve. Concentrations of lead as low as 0.01 part per million in the original sample and 60 parts per million in the ash have been measured. Repeat analyses on the same sample show an average deviation from the mean of approximately 15 percent when triplicate exposures are used. Tests indicate variations are due chiefly to the ashing and mixing processes. The method is rapid and entirely objective.

* Now at Montana State University, Missoula, Montana.

10. Contribution to the Theory of Liquids. AHLBORN WHEELER, *Shell Development Company, Emeryville, California. (Introduced by O. Beeck.)*—To date all theories of the liquid state have been seriously handicapped by the fact that we cannot assign the correct statistical weight (entropy) to a given arrangement (energy state) of the molecules in our system. It is shown how this can be done for the simplest type of liquid system: a linear chain of molecules with arbitrary interaction potential between nearest neighbors. The exact partition function is constructed for this system and the thermodynamic properties are calculated for potential functions of the Lennard-Jones type. The nucleus of the solution is an exponential integral of $(E+pV)/kT$ over the coordinate space, and this integral gives the Gibbs free energy directly. The results should be of considerable assistance in formulating improved theories for real liquids. First of all the form of the solution is very suggestive in indicating how to construct new and perhaps more accurate partition functions for the three-dimensional case. Secondly we have a "yardstick" with which to test the validity of any approximate model of a liquid. This model may be applied to our one-dimensional system, and the results compared with the exact solution.

11. Identification of Hydrocarbons by Means of Their Infra-Red Spectra. R. S. RASMUSSEN, R. R. BRATTAIN, AND O. BEECK, *Shell Development Company, Emeryville, California.*—Infra-red absorption spectroscopy in the rocksalt region (2–15μ) has been applied to the rapid qualitative and semi-quantitative analysis of higher isomeric paraffin and olefin hydrocarbons (C_6 to C_8). Spectra of pure hydrocarbons serve as comparisons, against which the spectra of new preparations are checked. Samples which are nearly pure are readily identified in this way, and the type and amount of impurity can be estimated. Since in complex mixtures the bands of the individual hydrocarbons often overlap to a great extent, a rough distillation may be necessary in order to divide the mixture into various cuts which in turn can be examined by the infra-red absorption method. Further use of infra-red spectra can be made in those cases where characteristic bands exist for specific groups. These bands may be used in establishing the structure of molecules. While this procedure is uncertain in the case of paraffin hydrocarbons, it has proved highly useful in the study of olefins. Thus the $C=CH_2$ group (α-position of the double bond) is indicated by a band at 3.2μ and a strong band in the 6μ region. Moreover, several very strong bands in the 10–12.5μ region are highly characteristic of the type of substitution around the double bond.

12. Quantitative Analysis of Multicomponent Mixtures by Means of Infra-Red Spectrophotometry. R. R. BRATTAIN, R. S. RASMUSSEN, AND A. M. CRAVATH, *Shell Development Company, Emeryville, California.*—Provided sufficient differences exist in the absorption spectra of the pure components and provided Beer's law is obeyed, spectrophotometric analysis of a multicomponent mixture of n components can be obtained by making optical density measurements at n wave-length positions, and solving n linear simultaneous equations in n unknowns. For routine work in the infra-red region from 2 to 15μ, desirable stability is gained by using wide spectral slits and no further amplification of the thermocouple output. Under these conditions Beer's law cannot be applied to the absorption measurements because of the rapid change of the true absorption coefficient over the spectral slit width. In order to analyze mixtures under these conditions, it is assumed that the optical density of the mixture is equal to the sum of the optical densities of the pure components, although the optical density of a component is no longer linear with concentration. Calibration curves can be obtained from data on pure compounds giving optical density as a function of concentration (non-linear) and can be used in the analysis of mixtures. The method has been thor-

oughly tested on a large number of hydrocarbon mixtures and was found to give excellent results with mixtures of 6 and 7 components. An accuracy of ±0.5 percent (of total sample) is obtained for each component. By using a specially devised rapid method of calculation the time required to analyze a six-component C_4 hydrocarbon mixture is 1½ hours as against 12 to 15 hours by low temperature distillation and subsequent gas analyses.

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